

a good bunsen flame and then for about half an hour in a blowpipe flame.

When cold, the solid cake is placed in a porcelain dish, the crucible being washed first with water and then with hydrochloric acid, the latter being then gradually added until the ferric and magnesium oxides are completely dissolved (10 grams of the mixture require about 45 c.c. of HCl of D 1.12). The liquid is afterwards evaporated to dryness and treated further as in the preceding method.

**2. Determination of the Carbon.**—With products not attacked by acids, the carbon should be estimated by direct combustion in a current of oxygen (*see* Iron, 1, *b*).

**3. Determination of the Manganese.**—(*a*) The hydrochloric acid solution obtained in the determination of the silicon as under 1, *a* or 1, *b* is placed in a measuring flask. The residue remaining after treatment of the silica with hydrofluoric and sulphuric acids is dissolved in hydrochloric acid or, if insoluble matter then remains, fused with sodium carbonate and the fused mass dissolved in hydrochloric acid. This solution is added to the other in the measuring flask, the whole made up to volume and the manganese titrated by Volhard's method (*see* Ferro-manganese).

(*b*) In presence of chromium or vanadium, 0.2–2 grams of the sample are fused with a mixture of sodium carbonate and magnesium oxide (*see* 1, *b*) and the product lixiviated with hot water (if the mass is green owing to the presence of manganates, these are reduced by addition of a small quantity of sodium peroxide, excess of which is decomposed by boiling for some time). The residue is collected on a filter, washed with hot water, dissolved in conc. hydrochloric acid, boiled to expel chlorine, and, when cool, made up to volume in a 250 c.c. measuring flask: in an aliquot part the manganese is estimated by Volhard's method (*see* Ferro-manganese).

**4. Determination of the Phosphorus.**—(*a*) An aliquot part of the hydrochloric acid solution obtained after elimination of the silica (*see* 1, *a* and *b*) is concentrated to a syrup and the phosphorus precipitated with the molybdate reagent (*see* Determination of phosphorus in iron).

(*b*) 1–3 grams of the sample are fused with the sodium carbonate-magnesia mixture (*see* 1, *b*), the product being dissolved in hydrochloric acid and the silica rendered insoluble and removed. The solution is then evaporated to dryness, the residue dissolved in nitric acid and the phosphoric acid precipitated with the molybdate reagent.

**5. Determination of the Sulphur.**—1–3 grams of the sample are fused with sodium carbonate and magnesia (*see* 1, *b*), the mass taken up in bromine water, the bromine expelled by boiling, hydrochloric acid added to dissolve the ferric oxide and magnesia, the silica rendered insoluble, the residue taken up in dilute hydrochloric acid and the silica having been

sulphur and, sometimes, calcium. Phosphorus is an injurious constituent, the maximum allowable limit being 0.15–0.2%. The mean percentage compositions of the commoner commercial forms are (Geiger) :

TABLE XV  
Compositions of Ferro-silicons

	I	II	III	IV	V	VI
. . .	25.89	29.66	51.80	53.75	51.20	75.67
. . .	72.92	72.99	47.30	45.09	48.89	23.01
. . .	0.52	—	0.30	0.11	—	0.31
. . .	0.42	0.56	0.35	0.11	0.37	0.26
. . .	0.03	0.01	0.02	0.005	0.007	0.01
. . .	0.04	0.30	0.04	0.041	0.04	0.04
. . .	—	0.30	—	0.60	0.17	—
. . .	—	0.25	—	—	—	—
. . .	—	—	—	0.04	—	—
. . .	—	—	—	0.05	0.21	—

## FERRO-MANGANESE AND SPIEGELEISEN

Ferro-manganese is usually obtained in the blast furnace from a mixture of iron and manganese minerals, and serves for the de-oxidation of steels and for the preparation of manganese steels and other special alloys. It is a greyish yellowish white, compact and with a granular structure intercrystalline, especially in the high percentage types, by bluish, iridescent, crystals.

Spiegeleisen is a form of white cast-iron very rich in manganese with a lamellar structure and a shining and sometimes iridescent surface ; it has the same uses as ferro-manganese.

The analyses of these products may include, besides the determination of manganese, also those of the carbon, silicon, phosphorus, sulphur, etc., which are always present in the commercial products in larger or smaller amounts.

**Determination of the Manganese.**—Numerous methods, gravimetric and electrolytic, have been proposed for the determination of the manganese in ferro-manganese and manganiferous cast-irons.

The following will be described : Volhard's volumetric method and its recent modifications introduced by Wolff, Schöffel and Donath, and the electrolytic method.

3.2 grams of the pure salt in boiled distilled water and making up to 1 litre.

(2) Sodium arsenite solution, obtained by dissolving 1.6 gram of pure arsenious anhydride and 0.8 gram of pure sodium hydroxide in water, heating if necessary, and making up to 1 litre: 1 c.c. of this solution corresponds with about 0.5 c.c. of the permanganate solution.

*Titration of the permanganate solution* (Sörensen). About 0.3 gram of pure sodium oxalate, in minute crystals and dried at 100°, is weighed exactly, dissolved in 500–600 c.c. of boiling water, mixed with 50 c.c. of dilute sulphuric acid (1 vol. acid to 5 vols. water) and the permanganate solution run in from a burette until a faint pink colour persists. Since 670 grams of sodium oxalate are equivalent, as regards permanganate, to 164.79 grams of manganese as salt, the amount of manganese,  $x$ , corresponding with the permanganate used is given by

$$670.0 : 164.79 :: P : x,$$

where  $P$  is the quantity of the oxalate taken. The quotient of  $x$  by the number of c.c. of permanganate used gives the amount of manganese corresponding with 1 c.c. of permanganate.<sup>1</sup>

*Procedure.* 1–2 grams of ferro-manganese or 2–5 grams of spiegeleisen are treated with nitric acid ( $D = 1.18$ ) according to the conditions described under 2 (p. 172). The solution is evaporated, ignited to decompose the nitrates, taken up in hydrochloric acid and the silica rendered insoluble, filtered and, if required, weighed. The hydrochloric acid solution, containing the manganese, when cold is made up to 250 or 500 c.c. in a measuring flask. The titration of the manganese is carried out on aliquot parts of the solution, each containing 0.04–0.08 gram of manganese.

If the sample is of high manganese content and hence contains too little iron, it is well to add to each portion 5–10 c.c. of ferric chloride solution (500 grams of pure ferric chloride dissolved in water acidified with hydrochloric acid and the volume made up to 1 litre). In this case it is necessary to ascertain, by a blank test under similar conditions, whether the ferric chloride absorbs permanganate and, if so, to allow for this in the calculation.

*Preliminary test.* Before titrating, a trial test must be made to establish the quantity of permanganate to be added.

An aliquot part of the solution is treated in a litre flask with a few drops of 30% hydrogen peroxide to oxidise any trace of ferrous salt and then heated to boiling to expel the excess of the oxidising agent. After 10–15 minutes' boiling, the volume is made up to 600–700 c.c. with boiling water, a suspension of zinc oxide<sup>2</sup> in water being then added in small amounts and with shaking until all the iron is precipitated in brown flocks (not pale

<sup>1</sup> The reaction between sodium oxalate and permanganate takes place thus:

liquid appears colourless.<sup>1</sup> The precipitate settles rapidly if held inclined in a suitable stand.

When the precipitate has deposited, 10 c.c. of the permanganate solution is added, the liquid shaken, the precipitate allowed to settle and, if the liquid is colourless, a further 10 c.c. of permanganate are added. The procedure being continued until the liquid contains excess of permanganate. The excess of permanganate is titrated with the sodium arsenite solution, which is added gradually and with shaking and with an equal volume of water after each addition until the liquid is decolorised. From the volume of permanganate used, less that corresponding with the arsenite solution, the amount of manganese is calculated (1 c.c. of arsenite = about 0.5 c.c. of permanganate), the permanganate required to oxidise the manganese completely is found and approximately.

2. For the actual titration of the manganese, an aliquot part of the solution equal to that used in the preliminary test is oxidised with potassium dichromate, boiled, diluted with boiling water to 600–700 c.c. and then potassium hydroxide is added to precipitate the iron.

When the precipitate is settling, the volume of permanganate found in the preliminary test plus 3–4 c.c. is introduced into a beaker and then rapidly poured into a flask, the latter being shaken and the beaker rinsed out with water. When the precipitate has settled again, the excess of permanganate added is determined by titration with the sodium arsenite as in the preliminary test. Next, in order to determine the true titre of the permanganate with respect to the permanganate under the exact conditions used, a known volume of 5 c.c. of the permanganate is added and the liquid decolorised by the arsenite solution. From these data a simple calculation gives the amount of permanganate required for the complete oxidation of the manganese, and hence the amount of the latter.

It is always advisable to carry out control determinations on different portions of the solution.

EXAMPLE. 1 c.c. of the permanganate solution is found to correspond to 0.5 gram of manganese. In the actual test, 35 c.c. of permanganate solution is added and the excess required 8 c.c. of arsenite solution, of which 9 c.c. of arsenite solution is equivalent to 5 c.c. of permanganate. Since

$$9 : 5 = 8 : 4.44,$$

the amount of permanganate reduced will be  $35 - 4.44 = 30.56$  c.c. and  $30.56 \times 0.5$  = amount of manganese in the aliquot part of the solution taken.

This method is used more especially in laboratories where estimations of manganese are made regularly; it is fairly exact and, the solutions being standard, is rapid. It cannot be used directly in presence of chromium, vanadium, cobalt, these also reducing the permanganate (for the determination of manganese in the presence of these elements, see the determination of



titration : the permanganate solution is added little by little to the boiling liquid and the precipitate allowed to settle after each addition, this being continued until the supernatant liquid exhibits a persistent pink colour. In this case, also, a preliminary trial titration is, of course, necessary. It appears, however, that under these conditions, intermediate oxides of manganese may be formed, so that the results are not always exact.

(b) ELECTROLYTIC DETERMINATION.<sup>1</sup>—1.5 gram of the finely powdered alloy is treated, in a covered porcelain beaker of about 100 c.c. capacity, with 30 c.c. of nitric acid (D 1.2) containing a few drops of hydrochloric acid. At the end of the action, the clock-glass and the edges of the beaker are washed with water, 1-2 grams of ammonium nitrate added and the liquid evaporated on a water-bath to a syrup and then carefully over a small direct flame to redness.

When cold, the oxides of iron and manganese are dissolved in 4-5 c.c. of conc. hydrochloric acid in the hot, 10 c.c. of 50% sulphuric acid being added to the cooled liquid and the solution heated on a sand-bath until the hydrochloric acid is completely expelled and copious white fumes appear. After being heated with water to dissolve the sulphates of iron and manganese, the liquid is filtered and the filtrate collected in a 250 c.c. measuring flask and the beaker and filter washed repeatedly with boiling water acidified with sulphuric acid.

The filter then contains the silica, contaminated by small quantities of graphitic carbon. If the silicon content is required, the procedure given on p. 171 is followed.

The liquid in the flask is made up to 250 c.c. and 50 c.c. (= 0.3 gram of the alloy)<sup>2</sup> treated in a 100 c.c. beaker with ammonia until the iron begins to precipitate. The liquid is then heated on a steam-bath and dilute sulphuric acid added drop by drop until the ferric hydroxide is completely dissolved. The solution of ferric and manganese sulphates is then poured into a solution of 6-7 grams of ammonium oxalate in a little boiling water contained in an electrolytic cell (not too narrow), 5-6 c.c. of 2% hydrazine sulphate solution being added and the liquid diluted to 200 c.c. and subjected to electrolysis to deposit the iron :  $ND_{100} = 0.7$  amp., voltage = 4-4.5, duration = 3-5 hours, Winkler electrodes (*see* later : Electrolytic analysis of metals).

When the electrolysis has commenced, 2% hydrazine sulphate solution is allowed to drop in the neighbourhood of the anode from a small tap-funnel drawn out to a capillary (8-10 drops per minute), this addition being continued uninterruptedly throughout the electrolysis.

As soon as the liquid loses its yellow tint and becomes completely colourless, a drop is removed, treated with a drop of dilute nitric acid, 2-3 c.c.

ed by the decomposition of the ammonium oxalate, to redissolve  
dioxide, and to reduce the volume to 60–70 c.c. The liquid  
ed with 1.5 gram of chrome alum and 10 grams of ammonium  
the hot solution filtered directly into the matte Classen capsule.  
of ammonia (D 0.94) have been added, the liquid is mixed,  
70–80° and subjected to electrolysis, the capsule being con-  
the positive pole.  $ND_{100} = 0.5-0.6$  amp., voltage = 2–3.  
e = 70–80°, duration = about 2 hours.

ne deposition is found to be complete by raising slightly the  
liquid, the disc functioning as cathode is lifted out and the  
the dish poured away, the deposited manganese dioxide being  
ashed with water. The dish is then dried at 100° and heated  
ed heat to transform the dioxide and the higher oxides into the  
e,  $Mn_3O_4$ .

old, the dish is washed once more with water to remove any  
d which may be included, again ignited and weighed rapidly  
the manganese oxide from absorbing moisture:  $Mn_3O_4 \times 0.7205$

rolytic method certainly takes longer than the volumetric method,  
advantage of not requiring standard solutions and of being applicable  
ence of chromium, cobalt, nickel and vanadium.

**Determination of the Carbon.**—This is usually carried out by the  
hod (*see* Iron, 1, *a*) or, better, by direct combustion in a current  
(*see* Iron, 1, *b*).

**Determination of the Silicon.**—When this is required, it may be  
ng with the determination of the manganese (*see* Determination  
n iron, 2, *b*).

**Determination of the Phosphorus, Sulphur and Arsenic.**—  
ents are estimated as in cast- or wrought-iron.

\*  
\* \*  
\*

manganese content of ferro-manganeses may vary from 25 to 85% and  
content from 5 to 7.5%, the two generally increasing together.  
anenes contain also 0.5–2.5% of silicon, small quantities of phosphorus  
and minimal traces of sulphur, copper, etc.  
isen contains 0.2–1.2% of silicon, 4–5% of carbon and 5–25% of  
and sometimes, as impurities, small proportions of phosphorus and

# SILICON FERRO-MANGANESE

## (Silico-spiegeleisen)

Silicon ferro-manganese may be regarded as a product intermediate between ferro-silicon and ferro-manganese. It is obtained in the blast furnace or the electric furnace, the latter yielding especially pure products. Its analysis includes the following:

**1. Determination of the Silicon.**—As silicon ferro-manganese is not attacked either not at all or with difficulty by acids, the silicon should be estimated by the methods given for the determination of silicon in ferro-silicon.

**2. Determination of the Manganese.**—As in ferro-silicon.

**3. Determination of the Carbon.**—By direct combustion in a stream of oxygen (*see* Iron, 1, b).

**4. Determination of the Phosphorus and Sulphur.**—As in ferro-silicon.

\*  
\* \*

Silicon ferro-manganese obtained from the blast furnace contains 20% Mn, 10–12% Si (occasionally 20%), 2–2.5% C, 0.01–0.2% P, and sometimes minimal traces of sulphur.

That from the electric furnace may contain 35–75% Mn, 20–35% Si, 0.6–1.0% C, 0.01–0.06% P, 0.02–0.03% S, and sometimes traces of copper, aluminium, and phosphorus.

## FERRO-CHROME

Ferro-chrome may be prepared in the blast furnace or the electric furnace and serves for making chrome steels. Its analysis includes the following:

**1. Determination of the Chromium.**—The sample is best analysed by the following methods.<sup>1</sup>

(a) **FUSION WITH SODIUM HYDROXIDE AND PEROXIDE.** 0.3–0.5 gram of the very finely powdered sample are mixed, in a silver crucible or dish, with a silver spatula, with 2 grams of sodium hydroxide in minute portions. As the mixture is heated, the reaction becomes more violent; the mixture being covered with 4 grams of sodium peroxide. The mixture is then heated to incipient fusion, the flame being then removed to prevent the reaction from becoming too violent; the heat developed in the reaction rapidly melts all the contents of the dish or crucible. A little more sodium peroxide is added to the fused mass, the latter being heated gradually to fusion when the reaction begins to abate. After about 10 minutes, 5 grams of sodium peroxide are mixed in and the mass heated rather energetically so as to maintain it in a state of quiet fusion for 20–30 minutes.

should then be completely attacked.  
 ON WITH SODIUM CARBONATE AND MAGNESIA. 0.3–0.5 gram of powdered sample is mixed with about 10 parts of a mixture of sodium carbonate and magnesium oxide, and the mixture heated in a crucible under the conditions prescribed for the analysis of (1, b).

*of the chromium.* The fused mass obtained by one of the above methods is lixiviated with water, as indicated on p. 183 (Chrome Steels), the scales formed being reduced with sodium peroxide, the liquid decanted to expel excess of sodium peroxide and made up to volume in a measuring flask; the chromium is then titrated iodometrically in 10 or 100 c.c. portions (*see* Chrome Steel).

Inspected that the attack of the metal has not been completed, the residue is lixiviated, dried, fused with sodium carbonate and the fused mass lixiviated, the resultant solution being added to that from the first

**Determination of the Carbon.**—This is effected by direct combustion in a current of oxygen (*see* Iron, 1, b).

**Determination of the Manganese.**—The residue obtained in the determination of the carbon with water of the fused mass is dissolved in hydrochloric acid as indicated under Ferro-silicon, 3.

**Determination of the Silicon, Phosphorus and Sulphur.**—As indicated under Ferro-chrome.

\*  
\* \*

Ferro-chrome contains 40–65% Cr (rarely 80%), quantities of carbon varying from 0.3 to 1.2% according to the degree of refining, and the ordinary impurities found in steel. Three grades are distinguished commercially:

1. Ferro-chrome No. 1 (0.3–0.75% C, 60% Cr).

2. Ferro-chrome No. 2 (1–2% C, 60% Cr).

3. Ferro-chrome (4–10% C, 60% Cr).

The following table gives the mean compositions of various ferro-chromes

TABLE XVI

### Composition of Ferro-chromes

Element	Cr	Fe	C	Si	Al	Mn	Ca	S	P
Ferro-chrome No. 1	54.50	22.00	0.50	2.25	0.80	0.15	0.25	0.04	0.03

Ferro-tungsten is obtained by the direct reduction of natural wolframite or scheelite with carbon in a crucible, or in the blast furnace or the electric furnace, and serves for the preparation of tungsten steels.

Ferro-tungsten and steels with high tungsten contents (20%) are insoluble or difficultly soluble in acids, and to attack them it is necessary to fuse with alkali. Their analysis includes :

**1. Determination of the Tungsten.**—0.5–2 grams of the finely powdered sample are fused with 10 parts of the mixture of sodium carbonate and magnesia, as under Ferro-silicon, 1 b, or 1 gram of the sample is fused with 4–5 grams of sodium-potassium carbonate and 0.5 g. of potassium nitrate. In either case, the product is lixiviated with hot water, sodium peroxide being added and the liquid boiled to destroy the excess of this reagent, if the solution appears greenish owing to the presence of manganates. The liquid, which contains the tungsten as sodium tungstate, is filtered into a 500 c.c. measuring flask and the residue repeatedly washed, dried and again fused with sodium carbonate, the mass being lixiviated with water to recover any small amount of tungsten which may have resisted the first attack.

An aliquot part (50 or 100 c.c.) of the total solution is acidified with hydrochloric acid, evaporated to dryness, heated at 135°, taken up with water, and reprecipitated with hydrochloric acid, etc., as described for the analysis of tungsten.

**2. Determination of the Carbon.**—With products insoluble in acids, direct oxidation in a current of oxygen must be employed (*see* Iron and Steel).

**3. Determination of the Silicon.**—The procedure employed for ferro-silicon is followed, but since tungstic acid separates with the silica, the latter is treated with hydrofluoric acid and estimated by the difference in weight (*see* Tungsten Steels).

**4. Determination of the Manganese.**—This is carried out on the residue remaining undissolved when the fused mass is lixiviated with water (*see* Ferro-silicon, 3).

**5. Determination of the Phosphorus and Sulphur.**—As in the case of ferro-silicon (*see* p. 196).

\* \* \*

Crucible ferro-tungsten contains, on the average, 25–30% W, 60–65% Fe, 1–1.5% C, with traces of manganese, phosphorus, etc.; that from the electric furnace always contains considerable proportions of manganese (in some cases up to 40%) and carbon (4–5%).

Ferro-tungsten obtained in the electric furnace usually has a high tungsten content (80–90% W, 10–20% Fe, very small amounts of carbon, silicon, and phosphorus).

23.29	1.75	0.33	0.80	0.06	—	0.01	0.01
—	1.36	0.33	0.43	0.09	Trace	0.01	0.007
—	0.38	0.13	—	—	Trace	0.07	0.009
22.0	—	0.3	0.8	—	—	0.01	0.02
15.72	0.52	0.13	—	—	—	0.01	0.01

## FERRO-VANADIUM

Vanadium is obtained exclusively by electro-thermal processes, in combination with aluminothermal processes, from mixtures of iron and vanadium oxide. They serve as deoxidising agents for pig-iron and steels, and for the preparation of vanadium

steel. To-day it is comparatively pure and, besides iron and vanadium, contains only small quantities of carbon and silicon and some of phosphorus and manganese. Its analysis includes :

**Determination of the Vanadium.**—1-2 grams of the sample are placed in a small porcelain dish with nitric acid (D 1.18), evaporated to dryness and the oxides obtained fused with sodium peroxide, the vanadium being extracted with water as indicated in the analysis of ferro-steel.<sup>1</sup>

The filtrates from the lixiviation are together made up to 500 c.c. and vanadium in an aliquot part determined as with vanadium steel.

**Determination of the Carbon and Silicon.**—As in ordinary cast-

**Determination of the Phosphorus.**—This is carried out on an aliquot of the 500 c.c. (*see* 1, above) by the method given for estimating phosphorus in the presence of vanadium (*see* Iron, 4, 3).

**Determination of the Manganese.**—As in ferro-silicon.

\* \*

Commercial types of ferro-vanadium contain 35-55% of vanadium, with 0.05-1.2% of silicon (0.09-1.2%) and carbon (1-3%) and traces of phosphorus, magnesium and aluminium.

The compositions of ferro-vanadiums made in the electric furnace are given in Table I (continued).

For the analysis of ferro-vanadium, the sample can be finely powdered, it may be fused at once with a mixture of sodium cyanide and magnesia (*see* p. 195), the mass obtained being lixiviated with

No.	V	Fe	C	Si	Al	Mn	Cu	S
1	55.0	40.00	4.00	0.30	0.10	0.30	—	0.03
2	52.8	45.84	1.04	0.09	—	—	—	0.025
3	47.4	51.20	1.07	0.09	—	0.07	0.01	0.009
4	34.1	64.22	1.42	0.12	0.12	0.12	—	0.03

## FERRO-MOLYBDENUM

This is obtained industrially by electro-thermal processes and is essentially, together with chromo-molybdenum and molybdenum, making molybdenum steels. The elements commonly estimated are molybdenum, carbon, silicon, manganese, phosphorus, sulphur and tungsten.

**1. Determination of the Molybdenum.**—1–2 grams of the powdered sample are heated at not too high a temperature with about 10 parts of the sodium carbonate and magnesia mixture, the semi-fused mass being extracted with hot water; these operations are then repeated until we can extract any small quantities of molybdenum remaining in the residue (see Chrome Steels). The two solutions together are made up to 500 c.c. in a measuring flask and the molybdenum in an aliquot part (50–100 c.c.) is determined as in molybdenum steels.

**2. Determination of the Carbon.**—By direct combustion in a stream of oxygen (see Iron, I, b).

**3. Determination of the Silicon, Manganese, Phosphorus and Sulphur.**—As in ferro-silicon.

**4. Determination of the Tungsten.**—In an aliquot part of the solution (c.c. of solution (see I, above)) the tungsten is determined as in ferro-tungsten.

\*\*\*

According to the character of the original ores, different types of ferro-molybdenum are obtained. These may contain 15–80% of molybdenum (usually 50–70%), from 0.5% (for the more refined products) to 5% of carbon, 0.1–0.5% of silicon and small quantities of manganese, sulphur, phosphorus and sometimes tungsten.

The commoner commercial products have the following mean composition (Guillet):

TABLE XIX  
Compositions of Ferro-molybdenum

--	--	--	--	--	--	--	--	--

mium is prepared by electro-thermal and alumino-thermal from rutile and from iron ores rich in titanium, and serves as a reagent in the refining of cast-iron and steel.

**Separation of the Titanium.**<sup>1</sup>—0.5 gram of the finely powdered titanium is heated in a platinum crucible and, after cooling, evaporated to dryness with a few c.c. of hydrofluoric acid. The residue is then heated to dryness in the same crucible with 5–7 grams of potassium bisulphate, the mass taken up in hydrochloric acid (not too dilute) and heated on a water-bath until solution is complete. The liquid is made up to 100 c.c. and mixed with 20–30 c.c. of concentrated sodium bisulphite. The solution is heated gently to reduce the iron to ferrous salts (a drop of potassium ferricyanide should give no appreciable colour with thiocyanate). When reduction is complete and the temperature of the liquid not above 60°C., ammonia in addition is made, in one quantity and with shaking, of 70% concentrated ammonia containing in solution 30 grams of potassium cyanide. The solution is then heated rapidly and kept near to the boiling point until the precipitate appears white and the supernatant liquid has a greenish-yellow coloration. When cold, the liquid is filtered and the precipitate washed, first with ammoniacal ammonium sulphite and then with hot water. The moist precipitate is dissolved in concentrated hydrochloric acid and the titanium oxide in the clear solution is precipitated by fresh addition of ammonia. The precipitate is filtered, washed, dried strongly and weighed:  $\text{TiO}_2 \times 0.6005 = \text{Ti}$ .

Aluminium occurs along with the titanium, the oxides thus fused with bisulphate, the fused mass dissolved in hydrochloric acid and the titanium separated from the aluminium by means of

**Separation of the Carbon.**—By direct combustion in a current of oxygen (see Iron, 1, b).

**Separation of the Silicon.**—0.3–1 gram is disintegrated with 10 c.c. of sodium carbonate and magnesia (see Ferro-silicon, 1, b, p. 10). When cold, the semi-fused mass is moistened with water, ground to a fine powder and poured into a beaker, the least possible quantity of rinsing water being used. The liquid is strongly acidified with hydrochloric acid and allowed to stand for 1–2 hours and then heated on a water-bath until the liquid becomes perfectly clear. The solution is evaporated to dryness with sulphuric acid, heated until copious white fumes appear, cooled and the separated silicon filtered off (see Ferro-silicon, 1, b).

**Separation of the Manganese, Phosphorus and Sulphur.**—The solution is treated with silicon



TABLE XX

## Composition of Ferro-titanium

No.	Fe	Ti	C	Si	Al	Mn	S
1	36.85	56.63	4.62	1.25	0.44	0.10	0.045
2	78.54	18.37	0.67	1.40	0.69	0.18	0.074
3	87.68	11.21	0.67	0.37	—	—	0.03

## FERRO-ALUMINIUM

Ferro-aluminium is usually prepared in the electric furnace by reducing alumina in presence of iron, and serves, like metallic aluminium—is much more used at the present time—as a deoxidising agent in the refining of cast-iron and steel. Its analysis includes:

**1. Determination of the Aluminium.**—Exact determination of aluminium necessitates preliminary expulsion of the iron by extraction with ether in Rothe's apparatus, the aluminium being then precipitated as phosphate.<sup>1</sup> When, however, very exact determination is not required, the following more rapid method (Regelsberger's) may be followed:

5 grams of the coarsely powdered sample are dissolved in a porcelain dish in dilute sulphuric acid (1:4), evaporated to dryness and heated in a sand-bath until white fumes are emitted. When cold the sulphate is dissolved in hot water and the solution poured into a 300 c.c. measuring flask, cooled, made up to volume, and filtered through a dry pleated filter into a dry vessel.

To 100 c.c. of the filtrate sodium bisulphite or hyposulphite is added until the iron is completely reduced (a drop of the liquid should give a blue colour with thiocyanate), the liquid cooled, most of the free acid neutralised with sodium carbonate, and the solution poured into a boiling mixture of 50 c.c. of sodium hydroxide solution (containing 10 grams of sodium hydroxide) with 40 c.c. of potassium cyanide solution (containing 8 grams of potassium cyanide).<sup>2</sup> When cold, the liquid is introduced into a 300 c.c. measuring flask, made up to volume, and filtered through a dry filter. To 300 c.c. of the filtrate (= 1 gram of the alloy), concentrated ammonium nitrate solution (15 grams in a little water) is added, the liquid being stirred to expel most of the ammonia, and the precipitated aluminium hydroxide filtered off, washed until the washing water no longer gives a blue colour

m, and titrated with permanganate ; the corresponding amount of iron is deducted from the total weight of the alumina.

**Determination of the Carbon, Silicon, Manganese, Phosphorus and Sulfur.**—As with iron (*see* p. 163).

The usual types of ferro-aluminium contain 10–20 % of aluminium.

## ELECTROLYTIC ANALYSIS OF METALS

The electrolytic method has now reached a high degree of accuracy and forms a valuable aid in the examination of metals and alloys. On account of their accuracy, their simplicity and their neatness, electrolytic methods have been given the preference over other methods, and a brief description of the necessary apparatus and a short outline of the conditions to be observed in the various operations will now be given.

**Currents of Current.**—The continuous current used should not be too variable but must be as far as possible constant. It may be obtained from primary batteries, accumulators, or the street mains.

Primary batteries do not answer very well the requirements of elec-

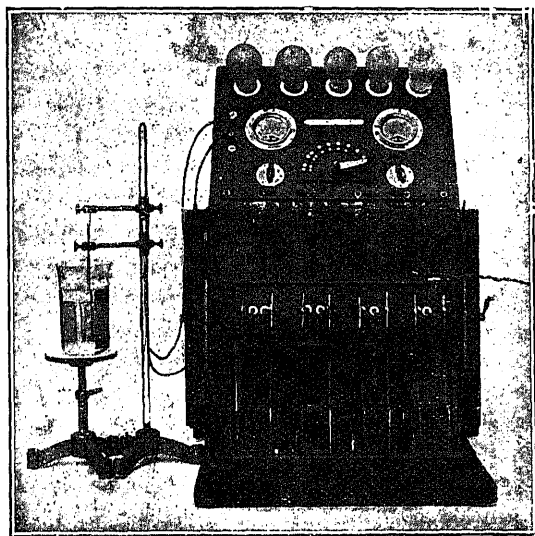


FIG. 16

lysis, since they usually yield a feeble current and must there-

size. For analysis with stationary electrodes, a battery of 4 elements of 30-50 ampere-hour capacity is sufficient, whilst rotating electrodes may require 12 accumulators of this capacity. The various elements should connect with either a mercury or plug commutator, so that they may be grouped readily in parallel or in series or in mixed formation according to circumstances.

The *electricity supply current* may also be used and, if continuous, requires only the insertion of suitable resistances. If alternating, it must be converted into continuous current by an electrolytic rectifier, which serves particularly well when only low current intensities are required (1-1.5 amp.).

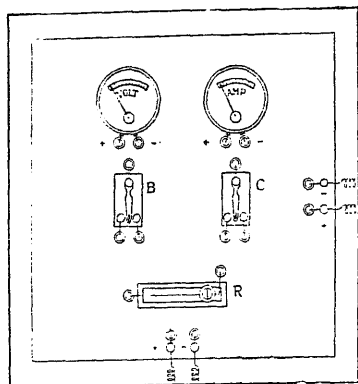


FIG. 17

regulate the current, an accurate amperemeter and voltmeter, a commutator *C* for inserting or cutting-out the amperemeter in the circuit including the electrolytic cell, and an interruptor *B* to insert at will the voltmeter and measure the pressure at the terminals. In any laboratory the current may be distributed in the form most convenient to the particular circumstances.

**3. Electrodes and Supports.**—In general the electrodes are of platinum or iridised platinum and that on which the metal is deposited, that is, the cathode, is of greater surface than the anode.

(a) WITH STATIONARY ELECTRODES. *Electrodes.* Of the numerous electrodes of different form and dimensions which have been suggested, those most suitable in practice are :

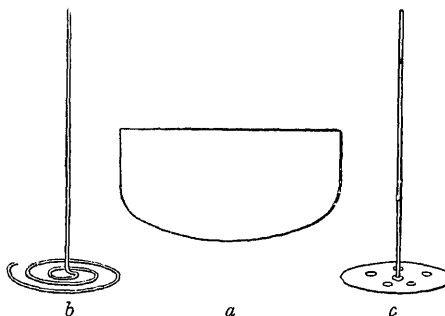


FIG. 18.

7 cases, especially when copper and iron are determined simultaneously, the central rod may be replaced with advantage by a glass cylinder of iridised, matte platinum 1.5 cm. in diameter and 5 cm. high (Fig. 19, *a*). This may hold as much as 0.3 gram of lead which is slowly deposited as peroxide, whilst the copper is deposited on the cathode.

The most convenient and the most reliable are those of Classen. They consist of a heavy iron foot carrying a thick vertical rod. To the insulating rod are fixed by pressure screws, the electrode holders,

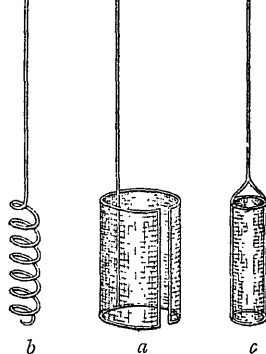


FIG. 19

Classen electrodes being a ring furnished with three platinum holders, which the dish rests on and a binding screw for suspending the whole. Those for Winkler electrodes two connecting screws (see Fig. 16).

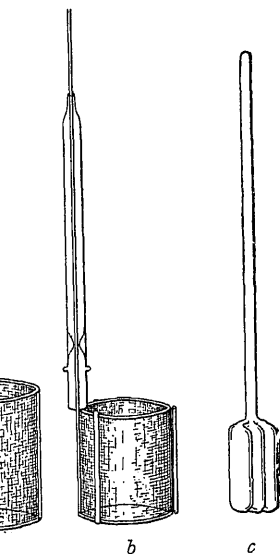


FIG. 20

(b) WITH ROTATING ELECTRODES. *Electrodes.* These may be: the Classen dish, within which the disc acting as anode revolves; or the Winkler cathode, inside which rotates a platinum spiral wound round a glass rod to give it solidity (Fig. 21). Other electrodes which are much in use and very convenient are those of Fischer, consisting of two concentric gauze cylinders (Fig. 20, *a*, *b*), insulated by quartz rods; the electrodes remain stationary, the liquid being kept in motion by a glass stirrer (Fig. 20, *c*) revolving inside the smaller cylinder.

*Stands.* These, besides supporting the electrodes, should permit of the rotation of one of the electrodes or of a stirrer. In its simplest form, a rotating electrode is shown in Fig. 21. One of the screws of the stand is replaced by a support carrying a rotating axis on which the

anode is fixed. The rotation may be imparted by a water turbine or an electric motor of adjustable speed. Much more perfect is the Fischer stand made for his electrodes and suitable also for use with the Classen dish (Fig. 22).

Another means for obtaining the rotation of the electrolyte is that pro-

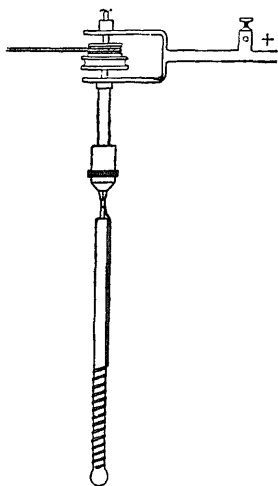


FIG. 21.

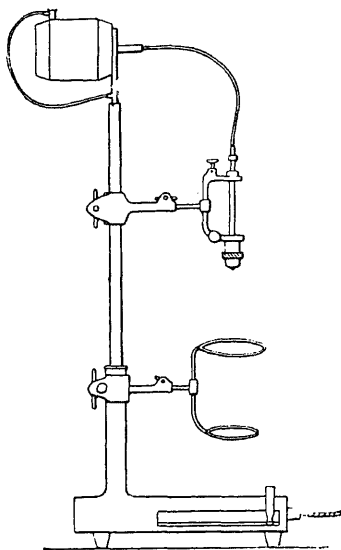
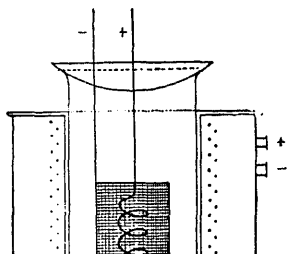


FIG. 22.

posed by Frary and based on the principle that any conductor carrying a current and situate in a magnetic field tends to move with a velocity depending on the intensities of the current and of the magnetic field. The arrangement of the apparatus is shown in Fig. 23. In practice, preference is given to mechanical methods of agitation.



**Practical Rules.**—When use is made of Winkler's electrodes, which are the most practical, the electrolysis is carried out in a beaker which is fairly tall and not too narrow. The prescribed reagents are added, suitably diluted so that the electrodes remain completely immersed, and mixed. The beaker is

adjusted to give the maximum resistance, the current started, the ammeter and voltmeter inserted in the circuit, and the rheostat regulated until the measuring instruments indicate the proper voltage; the instruments are then cut out.

In the Classen capsule the same directions are to be followed. The electrolyte is placed on the proper stand, the anode centrally and a few centimetres from the bottom, the cover fitted as above.

When rotating electrodes are used, the procedure is the same: when the covers are in place, the rotating apparatus is started so as to give the desired velocity (number of turns per minute), the cover fitted, the current regulated and the electrolysis continued.

**End of the Deposition.**—When the prescribed time for the deposition of the metal to be determined should be completed, it is ascertained if this is so, two means are used: (1) If the deposited metal is different in colour from platinum (e.g., copper), the level of the electrolyte is raised a few millimetres by addition of water; if, after some minutes, the newly immersed part of the electrode shows no deposit of the metal being determined, the deposition is complete. (2) A fresh portion of electrolyte is removed and tested for the metal by its most characteristic reactions.

**Washing of the Electrodes.**—With Winkler electrodes, the washing is done in the Classen capsule. The covers and thermometer are removed and washed with distilled water. The beaker is grasped in the left hand and the supporting stand held without interrupting the current. The beaker is then rapidly lowered and replaced by a small beaker, which contains, under the same circumstances, distilled water or water acidified with sulphuric acid. The beaker is supported on the stand. After 10–15 minutes the cathode is washed by a gentle jet of distilled water, then with alcohol and ether, dried in an oven at 60–70°, cooled in a desiccator and weighed.

In the Classen dish two cases present themselves. If the electrolyte is a powerful energetic solvent action on the deposited metal, the covers are removed, the anode detached and placed in a beaker which is kept near, the cathode being emptied into the same beaker and washed with a little water. The electrolyte is then completed with water, alcohol and ether, and the dish is dried at 70–75°, cooled in a desiccator and weighed. If, however, the electrolyte is not an acid, it may attack the metallic deposit during these manipulations. In this case, the washing should be carried out without interrupting the current.

A small stream of distilled water is passed into the dish by means of a Mariotte's bottle or otherwise, while at the same time the liquid

usual washing and drying of the cathode effected.

**Dissolution of the Metallic Deposits.**—Deposits of copper, zinc, nickel, silver, etc., are dissolved in nitric acid ; tin and iron in hydrochloric acid ; antimony in nitric acid containing a little tartaric acid in solution ; lead peroxide in nitric acid with a little oxalic acid dissolved in it ; manganous-manganic oxide in dilute sulphuric acid containing hydrogen peroxide. When Winkler electrodes are used, it is very convenient to immerse them in a tall, narrow vessel fitted with a ground stopper and containing the proper acid, which may be used repeatedly.

## COPPER AND ITS ALLOYS

The more important commercial products are : refined and electrolytic copper and its various alloys with phosphorus, silicon, manganese, zinc, tin and nickel.

After the usual tests for industrial copper, methods for the analysis of its principal alloys will be given, beginning with alloys of copper with phosphorus, silicon and manganese, and coming later to the most important ones, namely, the ordinary and special brasses and the ordinary and special bronzes.

Alloys of copper with nickel and zinc (argentan) will be treated along with nickel and its alloys, and its alloys with tin and antimony (anti-friction metals) along with tin and its alloys.

## COPPER

The complete analysis of commercial copper, that is, the determination of the copper and of all the extraneous elements accompanying it in large or small proportions (Bi, Pb, Sb, As, Sn, Ag, Au, Fe, Ni, Co, Zn, S, Se, Te, C, P, Si, O, etc.) is a very long and delicate operation.<sup>1</sup> Beyond a determination of the copper, commercial analyses as a rule require only estimations of the more injurious elements, especially of bismuth, arsenic, phosphorus, antimony, lead, sulphur, nickel, iron and oxygen. Rapid and exact methods for determining these elements will, therefore, be given.

**1. Determination of the Copper** (by *electrolysis*).—5 grams of the metal in fine turnings, freed from fat by means of ether and from traces of iron from the sampling tool by means of a magnet, are placed in a tall, narrow beaker covered with a clock-glass or with an inverted funnel of rather less diameter than the mouth of the beaker. The metal is there covered with water and treated with 5–7 c.c. of conc. sulphuric acid and

p., using Winkler electrodes; duration, 12-15 hours.

When the deposition is complete (*see* p. 213), the electrolytic beaker is removed without interrupting the current, by another small beaker containing water faintly acidified with sulphuric acid, the cathode being removed after some time and washed first with water, then with alcohol, and finally with ether; it is then dried at 70° and weighed. The increased weight represents copper and any silver present; the latter metal is determined by the method on p. 9 (below).<sup>1</sup>

If the copper deposited is not of a good, brilliant colour, but appears dull and spotted (presence of arsenic or bismuth), it is redissolved in 5-7 c.c. of conc. sulphuric acid and 15-20 c.c. of nitric acid diluted to 250-300 c.c. and again electrolysed with addition of a small amount of red lead sulphate (0.4 gram) and ferric sulphate (0.5 gram) to remove traces of arsenic and bismuth from being deposited with the copper.

The final liquid free from copper, together with the wash water, is used for the determination of antimony (*see* 5).

**Determination of the Bismuth.**<sup>2</sup>—(a) ELECTROLYTICALLY. 10 c.c. of the sample are dissolved in 50 c.c. of nitric acid (D 1.33), 10 c.c. of water being added when the action is complete and the solution concentrated to dryness. The residue is taken up in 200 c.c. of water containing 10 c.c. of sulphuric acid, the liquid being heated to boiling and the residue filtered and treated with 10 c.c. of phosphoric acid (D 1.71). When cold, the liquid is mixed with 30 c.c. of alcohol and, after 12 hours, filtered by decantation. The precipitate, which contains all the lead and bismuth of the sample, is washed first with a solution containing by volume about 1% of phosphoric acid, 5% of phosphoric acid and 15% of alcohol, and then with a solution of ammonium sulphide and potassium cyanide<sup>3</sup> to remove traces of copper, arsenic, antimony, etc. The precipitate is then washed with water, the hot liquid decanted, the residue washed with nitric acid diluted with an equal volume of water, filtered by decantation and the residue treated with aqua regia. The liquid is diluted with an equal volume of water, filtered and washed with boiling water. The solution is evaporated with 12 c.c. of sulphuric acid until the white fumes of sulphuric acid appear and, when cold, is treated

with a solution of large quantities of silver, the electrolysis should be started at 30° with a current of 0.1 amp. to deposit all the silver first. After some hours the current is increased to 0.5-1 amp. and the electrolysis continued at the ordinary temperature until all the copper is deposited.

(b) BY CHEMICAL MEANS (Abel and Field).—About 6 grams of the sample are dissolved in nitric acid, treated with about 0.3 gram of lead nitrate dissolved in a little water, the solution is alkaline and with a little ammonium carbonate. After a little while, the liquid is filtered, the precipitate washed with ammonia-water, dried, and weighed.



filtered, the filter washed with water acidified with sulphuric acid and containing alcohol (in all 35 c.c. of alcohol should be used) and the liquid, about 300 c.c. in volume, electrolysed to determine the bismuth.<sup>1</sup>  $ND_{100}$ , i.e., current per 100 sq. cm. of electrode surface, = 0.1 amp.; duration = about 48 hours; maximum quantity of bismuth which can be deposited = 0.1 gram.

(b) GRAVIMETRICALLY.<sup>2</sup> 10 grams of the sample are dissolved in 60 c.c. of nitric acid (D 1.3) and the excess of acid expelled by evaporation on a water-bath. The residue is dissolved in 400 c.c. of water and neutralised, with continual shaking, by means of a very dilute solution of sodium hydroxide. As the acidity diminishes, more and more dilute alkali should be used in order to prevent separation of large clots of copper hydroxide. A slight excess of the alkali is added so as to produce a faint permanent turbidity, the liquid being made up to a litre and heated for an hour on the water-bath, a few drops of the alkali solution being added should the turbidity tend to disappear. A little further sodium hydroxide solution is then added to form a just perceptible precipitate and, after 15–20 hours, the precipitate—containing, besides copper, all the bismuth, iron, etc., of the sample—is collected on a filter, washed with cold water and dissolved in hot dilute hydrochloric acid. The bismuth is precipitated by rendering alkaline with ammonia, the excess of which is expelled on the water-bath (the copper should not precipitate), and the precipitate filtered off and washed with hot water. The precipitated bismuth hydroxide is redissolved in hydrochloric acid, the liquid diluted and precipitated with hydrogen sulphide, the precipitate filtered off and washed with yellow ammonium sulphide to dissolve any traces of antimony present and then with water. The bismuth sulphide is then dissolved in nitric acid and reprecipitated with ammonia, the precipitate filtered off, washed, dissolved in nitric acid and the solution evaporated in a tared porcelain crucible, the bismuth oxide being gently heated and weighed:  $Bi_2O_3 \times 0.8965 = Bi$ .

**3. Determination of the Arsenic.**—5 grams of the sample<sup>3</sup> in fine borings are introduced into the flask used for arsenic distillation (see Iron, 6) and are gently shaken while 100–125 c.c. of conc. hydrochloric acid containing in solution 50 grams of ferric chloride free from arsenic<sup>4</sup> are added through a long-stemmed funnel. The flask is closed with the stopper carrying the pressure-regulating apparatus, connected with the pipette dipping into the ammonia solution, and heated gently to dissolve the metal completely; the flame is then increased and distillation carried on until the ammoniacal solution becomes faintly acid. At this point the distillation is suspended, the pipette removed and washed, and the arsenic determined iodometrically as indicated on p. 170.

1 c.c. of ferric chloride solution free from phosphorus and arsenic, the excess of the latter expelled, and the liquid diluted with ammonia. The precipitate is filtered off, washed with hydrochloric acid, and the acid solution treated as described if in presence of arsenic, on p. 176.

**Separation of the Antimony (Classen).**—The solution from which copper has been removed electrolytically as in 1, together with the water from the small beaker, is evaporated until the nitric acid is completely expelled; if the anode is brown, it is kept immersed for a few drops of hydrogen peroxide being added to dissolve the antimony deposited on it.<sup>1</sup> The solution is diluted with water and subjected to the action of hydrogen sulphide in the cold to prevent the precipitation of the arsenic. The precipitate is filtered off and washed, and the antimony oxide and sulphide and any tin oxide and sulphide dissolved in a sodium sulphide solution (D 1.225), 4–5 grams of potassium cyanide added to the solution and the latter electrolysed in the Classen cell,  $i = 0.15$  amp.; duration = 10–15 hours.

**Separation of the Lead (by electrolysis).**—5 grams of the sample is treated with 20–30 c.c. of nitric acid (D 1.18), the nitrous fumes are expelled by boiling and the liquid diluted to 250–300 c.c. and electrolysed, using a platinum cathode and a tared gauze cylinder anode, as described on p. 176,  $i = 0.5$ –1 amp., duration = 10–15 hours.

Copper is deposited on the cathode, lead is deposited as peroxide on the anode. At the end of the electrolysis, the electrodes are removed, washed with water, and the anode, after further washing with distilled water, dried at 180–200°, cooled and weighed:  $\text{PbO}_2 \times 0.866 = \text{Pb}$ . These and considerable quantities of bismuth and iron are also deposited. Amounts of the oxides of these metals are deposited on the anode with the lead peroxide. In such case the deposit is dissolved in dilute nitric acid containing a little alcohol, the solution being evaporated with the alcohol until copious white fumes appear, the residue being taken up with a little alcohol added, and the lead sulphate separated and weighed. Another method consists in employing, for the determination of lead, the lead sulphate which separates during the necessary preliminary electrolytic determination of the bismuth (*see 2, a*).

**Separation of the Sulphur.**—The solution freed from copper by electrolysis (*see 6*) is evaporated to dryness (to fix the sulphuric acid, it is advisable to add a little sodium carbonate). The residue is taken up with hydrochloric acid, the liquid being evaporated to dryness each time. The whole of the nitric acid. The final residue is then dissolved in conc. hydrochloric acid and 50 c.c. of hot water and barium

the evaporating liquid, the peroxides deposited on it being caused to solve by addition of a few drops of hydrogen peroxide. When the residue is dissolved in water and the solution treated in the hot with hydrogen sulphide to precipitate the arsenic, lead, antimony, etc. The precipitate is filtered off and washed, and the filtrate boiled to expel the hydrogen sulphide, treated with 1-2 c.c. of hydrogen peroxide, boiled and rendered alkaline with ammonia to precipitate the iron. When considerable quantities of iron are present, it is advisable to repeat this precipitation. The solution of the precipitate in a little hot, dilute sulphuric acid. The hydroxide separated is washed, dried and ignited; it may be weighed directly or dissolved in a little dilute sulphuric acid and estimated volumetrically (*see* p. 200).

The filtrate, or the mixed filtrates from the two precipitations, is used for the electrolytic determination of the nickel and zinc. First, 30 c.c. of ammonia and a few crystals of hydroxylamine sulphate are added. When the nickel then deposited, the zinc being determined in the residual solution (*see* Analysis of Argentan).

When determination of the zinc is not required, the nickel may be precipitated directly in the iron-free alkaline solution by alcoholic diglyoxime solution (*see* Gravimetric Analysis of Argentan).

**9. Determination of the Silver.**—2.5 grams of the sample are dissolved in 100 c.c. of nitric acid diluted with an equal volume of water. The solution being boiled to expel nitrous vapours and, without filtering, cooled to 95° and treated with a few drops of hydrochloric acid to precipitate the silver. The liquid is heated on the water-bath to separate the precipitate which is filtered off and washed with hot water, the silver being determined in this impure silver chloride either electrolytically or gravimetrically.

(a) **ELECTROLYTIC METHOD.** The precipitate is dissolved in 120 c.c. of 10% potassium cyanide solution, then diluted to 250 c.c. and electrolysed with a current of 0.1 ampere.

(b) **GRAVIMETRIC METHOD.** The silver chloride is dissolved in 100 c.c. of water by digestion in the hot for some time, the solution being filtered and treated with nitric acid to reprecipitate the silver chloride, which is weighed as usual.

**10. Determination of the Total Oxygen.**—The oxygen present in commercial copper occurs largely as cuprous oxide and partly in combination with extraneous metals. It is determined by causing it to combine with hydrogen at a high temperature and estimating the water produced. A condition essential to accuracy is that the hydrogen must be perfectly dry and free from oxygen.

containing prismatic asbestos heated to redness, the water absorbed by means of a U-tube charged with phosphoric

the determination, a blank test is made, the hydrogen being in the glass or porcelain tube to be used in the determination on a combustion furnace; after about 10 minutes, a tared phosphoric anhydride tube, full of hydrogen and connected with a calcium chloride tube to keep atmospheric moisture away, is attached, the tube heated to redness and the stream of hydrogen continued for 10 minutes. At the end of this time the burners are extinguished and the apparatus is allowed to cool in the current of hydrogen; the U-tube should show a perceptible increase in weight.

For the determination, 10 grams of the sample, freed from grease and dried in iron (see 1) are weighed in a perfectly dry porcelain boat, heated in the cold, dry combustion tube, the air being then expelled with hydrogen for 10-15 minutes. The phosphoric anhydride tube and the calcium chloride tube are then attached and the tube heated strongly for 20-30 minutes.

When the reduction is complete, the tube is allowed to cool in the current of hydrogen and the phosphoric anhydride tube weighed; the increased weight represents the water, and this should correspond with the oxygen lost from the sample in the boat.

The determination of oxygen in copper is a very delicate and perhaps not a very accurate operation. Metallographic examination gives information in this

\*  
\* \*

Good quality should be bright red and very ductile and malleable; it should be finely granular, of uniform colour and free from spots; its specific gravity should lie between 8.65 and 8.93, and it should contain more than 99% copper (electrolytic copper may contain 99.8-99.9% or even more). As the impurity diminishes, the specific gravity, malleability and ductility

decreases. Impurities, those of special influence on the mechanical properties are bismuth, lead, antimony, sulphur, arsenic, phosphorus, nickel, iron

and tin. Hampe, the presence of 0.02% Bi is sufficient to render copper brittle in the cold, while 0.05% makes it brittle also in the cold. Keller states that the presence of a few thousandths of bismuth is unsuitable for electrical purposes. A similar effect is exerted by lead in the proportion of 0.3-0.4%. Arsenic is once regarded as highly injurious, but less than 0.5% appears to be harmless in whatever proportion, it lowers the electrical conductivity, and antimony is unfit for making brass. Sulphur, which may be present in the form of free sulphide, renders it cold short if present in greater quantity

TABLE XXI

## Compositions of Commercial Copper

ce.	Cu	Bi	As	Sb	Pb	Fe	Ni + Co	Ag
(6 samples).	99.74-99.96	0.0-0.1	0.009-0.037	0.0-0.088	0-trace	trace-0.008	0.0-0.012	0.027-0.112
amples)	99.19-99.51	—	0.025-0.061	—	0.006-0.206	trace-0.037	0.279-0.467	0.014-0.028
) . . .	99.325	0.052	0.130	0.095	0.061	0.063	0.076	0.072
is) . . .	97.66-99.91	trace-0.53	0.009-0.094	0.00-0.102	0.0-0.042	trace-1.248	0.005-0.413	0.009-0.084
es) . . .	98.22-99.80	0.0-0.003	0.009-0.077	trace-0.088	0.0-0.05	0.006-0.038	0.02-0.08	0.014-0.113
coppers							.	
r) . . .	99.947	0.004	0.008	0.026	—	0.006	0.009	—
ishi) . . .	99.983	trace	—	0.012	—	trace	—	—
(O-Montana)	99.835	—	—	0.010	trace	0.004	0.007	—
r) . . .	99.989 <sup>1</sup>	—	0.00022	0.00065	—	—	—	0.00005
r) . . .	99.910 <sup>1</sup>	0.0017	0.01040	0.02730	trace	—	—	0.00004

<sup>1</sup> By difference.

copper is usually employed as a deoxidiser and for the preparation of bronzes. It occurs mostly in cakes of metallic appearance or steel-grey colour and sometimes with bluish reflections; and has a crystalline structure.

It comprises essentially determinations of the phosphorus. The impurities, derived from those of the copper used in its preparation, may be estimated by the methods given on p. 214 for the estimation of commercial copper.

**Determination of the Phosphorus.**—0.5 gram of the finely powdered sample is treated in a covered dish with 10 c.c. of nitric acid (D 1.4), being applied when the action slackens. If any unattacked residue remains after about 30 minutes, a few drops of hydrochloric acid are added and the liquid heated until solution is complete. The solution is evaporated to dryness with 10 c.c. of nitric acid. The residue is extracted with hot water acidified with nitric acid and the liquid filtered and dried (to determine, if necessary) any traces of silica present, the residue being made up to 250 c.c.

The filtrate and this solution are evaporated to 10 c.c. and treated with ammonium molybdate solution, the remaining procedure being as for the determination of phosphorus in iron (*q.v.*).

**Determination of the Copper.**—1 gram of the sample is treated with 10 c.c. of nitric acid (D 1.2) and 5 c.c. of hydrochloric acid in a covered dish. The solution is evaporated with 2–3 c.c. of sulphuric acid until the white fumes of hydrochloric acids are completely expelled and then heated until white fumes of sulphuric acid appear. When cooled, the residue is taken up in hot water, the solution being mixed with 5–6 c.c. of nitric acid (D 1.4), made up to 200–250 c.c. and electrolysed (*see* p. 214):  $ND_{100} = 0.3\text{--}0.4$  amp.; duration = 10–15 hours.

Copper usually contains 9–15% P (sometimes, however, only 0.5–1% P) and is given in practice to products with 10% P.

## CUPRO-SILICON

Cuprosilicon or copper silicide, also improperly termed silicon bronze, is prepared in the electric furnace by reducing silica with carbon in presence of copper. It is used especially for the deoxidation of bronzes and brassy alloys. The preparation of copper-silicon alloys containing small quantities of copper is used in electro-technics for telephone wires, cables, etc. (alloys of copper and Si).

For the estimation of the silicon and copper in cuprosilicon, see essentially determinations of the silicon and

1. **Determination of the Silicon.**—1 gram of the finely powdered sample is treated with 10–20 c.c. of nitric acid (D 1.4) and heated for a long time. After addition of 1–2 c.c. of hydrochloric acid, it is again heated for a short time and finally evaporated in presence of 2 c.c. of sulphuric acid. The heating is continued on a sand-bath until copious white fumes of sulphuric acid are emitted, the cooled residue being treated with water, filtered, and the filter thoroughly washed with hot water and with sulphuric acid. The filter, still somewhat moist, is placed upwards in a platinum crucible and the latter covered and heated gently and later to ignition, the subsequent procedure being that in estimating silicon in iron or steel (*see* p. 171).

2. **Determination of the Copper.**—The filtrate from the acidified with 5–6 c.c. of nitric acid, made up to 250–300 c.c. and electrolysed to determine the copper. Winkler electrodes;  $ND_{100} = 0.3-0.4$  amp.; duration, 10–15 hours.

The commoner commercial types of cupro-silicon contain 10, 15, 20 or 30 per cent of silicon.

## CUPRO-MANGANESE

The copper-manganese alloys are used as deoxidisers of copper for the preparation of copper-manganese alloys with a low content of manganese—so-called manganese bronzes—and of the manganese bronzes—true manganese bronzes. Analysis includes determination of the copper and manganese and, sometimes, of the impurities, particularly the lead, iron and nickel.

1. **Determination of the Copper.**—1 gram of the sample is placed in a covered dish with 10–15 c.c. of nitric acid (D 1.2), 6 c.c. of dilute sulphuric acid (1 vol. acid to 1 vol. water) being added when the reaction is complete and the liquid evaporated on a water-bath to eliminate the nitric acid and then heated on a sand-bath until copious white fumes of sulphuric acid appear. When cool, the residue is stirred and gently heated with 30 c.c. of water to dissolve the copper and manganese sulphates, 95% alcohol being added and the mixture left for one or two hours. The insoluble residue, consisting usually of silica and lead sulphate, is filtered off and washed with a mixture of 60 c.c. of water, 10 c.c. of alcohol and 10 c.c. of sulphuric acid, the filtrate being evaporated almost to dryness to expel all the alcohol, and the residue taken up in water, diluted to 100 c.c., heated to 60–70° and electrolysed to determine the copper: Winkler electrodes; temperature = 60–70°;  $ND_{100} = 0.2-0.3$  amp.; duration,

anode being kept immersed to dissolve the coating of manganese. The liquid is boiled for a few moments, the electrode washed with water and the solution, when cold, made up in a 300 c.c. flask. In aliquot parts the iron and manganese are determined either volumetrically or electrolytically.

**VOLUMETRIC METHOD.** In 50 or 100 c.c. the iron is determined by potassium permanganate after reduction with amalgamated zinc.<sup>1</sup> In an aliquot part (50 or 100 c.c. according to the amount of manganese present) the manganese is titrated by Volhard's volumetric method (*see* Volhard's method).

**ELECTROLYTIC METHOD.** In 100–200 c.c., according to the amount of manganese present, the iron and manganese are estimated as described in the electrolytic method.

**Determination of the Nickel.**—In an aliquot part of the 300 c.c. solution (see 2), the nickel is determined by means of dimethylglyoxime and the necessary quantity of tartaric acid (*see* Nickel Steel).

**Determination of the Silicon and Lead.**—The residue remaining after the copper and manganese sulphates are taken up in nitric acid contains all the silicon and lead of the sample as silica and lead.

The latter is now dissolved in nitric acid containing ammonium nitrate and the lead in the solution determined electrolytically in an ammonium nitrate solution (see Lead-tin Alloys).

The insoluble residue in nitric acid and ammonium nitrate consists of silica (or impure) and is filtered off, washed, ignited in a platinum crucible, treated with hydrofluoric acid and again weighed; the residue represents silica (*see* Determination of Silicon in Iron).

For copper-manganese alloys containing little manganese (manganese less than 5%), it is advisable to determine the copper separately in two distinct portions (each) of the sample. When the copper is eliminated, the two portions of manganese dioxide on the anodes are dissolved and made up together

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Alloys of iron and manganese containing about 25–30% of manganese with small amounts of silicon, etc. Two principal types are met with commercially: (1) a pure alloy with 72–74% Cu, 23–24% Mn, 2.5–4.5% Fe and 0.2–0.5% Si; (2) a pure alloy with 70–72% Cu, 28–30% Mn, 0.1–0.3% Fe and 0.05–0.1% Si.

Alloys with a low manganese content or *manganese bronzes*, used, owing to their strength and resistance to corrosion, for valves, tie-rods for locomotives, etc., contain on the average 10–15% Mn and such impurities as are usually met with in commercial



Ordinary brasses are alloys of copper and zinc in various proportions, always containing as impurities small quantities of lead, iron, tin and sometimes nickel, arsenic, sulphur, phosphorus and bismuth. Their analysis comprises the determination, by electrolytic or gravimetric methods, of the constituent elements and impurities.

## A. Electrolytic Methods

In a covered beaker, tall and narrow, 1 gram of the alloy in turnings form is dissolved at a gentle heat in 15 c.c. of nitric acid (D 1.2).

**1. Determination of the Tin.**—The solution is diluted with 30 c.c. of water and if it appears turbid owing to the presence of metastannic acid it is evaporated to dryness, taken up in a few drops of nitric acid and a little water, heated for some time and filtered, the insoluble residue being collected on a small, tight filter and the filtrate in a 350 c.c. electrolytic beaker. The filter is washed, first with water faintly acidified with nitric acid and then with water alone, dried, ignited in a porcelain crucible and weighed:  $\text{SnO}_2 \times 0.7881 = \text{Sn}$ .

**2. Determination of the Copper and Lead.**—The liquid free from the metastannic acid is treated with 15 c.c. of nitric acid of D 1.2 (in case of tin, it is not necessary to add fresh acid, since the evaporation of the solution to dryness is omitted), made up to about 200 c.c., allowed to stand and electrolysed to determine simultaneously the copper and the lead. The Winkler cathode and matte gauze cylinder anode;  $\text{ND}_{100} = 0.3$  voltage, 1.8–2; duration, 10–15 hours. After half an hour or an hour when the greater part of the lead has been deposited as peroxide on the anode, 20 c.c. of 10% sulphuric acid are added to the electrolyte, which is carefully stirred by means of a glass rod.

When the deposition of the copper and lead is complete, the electrolytic beaker is replaced, rapidly and without interruption of the current, by a small, tall and narrow beaker containing water acidified with sulphuric acid, this being replaced after some time by another beaker containing distilled water. Finally the electrodes are detached and washed, the cathode with water, alcohol and ether, followed by drying at  $70^\circ$ , and the anode with water alone, followed by drying at  $180\text{--}200^\circ$ :  $\text{PbO}_2 \times 0.866 = \text{Pb}$ .

**3. Determination of the Iron and Zinc.**—The liquid from the electrolytic beaker, after the copper and lead have been separated and the wash water from the first beaker are evaporated together until white fumes of sulphuric acid are emitted, in order to convert the zinc and iron nitrates into sulphates. When cold, it is taken up in water acidified with sulphuric acid, a few

phates and the clear, hot solution treated with ammonia in After a short rest on the water-bath, the precipitated ferric filtered off, washed, dried, ignited and weighed  $1: \text{Fe}_2\text{O}_3 \times$

now contains only the zinc, which may be estimated with rotating electrodes in the manner described below. In any if the brass contains more than 20% of zinc (shown by the er obtained), it is advisable to make up the volume of the 0 c.c. and to determine the zinc on 150 c.c.<sup>2</sup>

*Estimation with stationary electrodes.* The ammoniacal solution ch lactic acid, then rendered faintly alkaline with sodium ated with 3 grams of ammonium oxalate and 5 grams of e, heated gently to dissolve the salts and made up to about c. of lactic acid are then added and the still tepid liquid *coppered* Winkler cathode<sup>3</sup>; Winkler spiral anode; ND<sub>100</sub> 0.; voltage = 3-4; duration, 3-4 hours. After about 2 ent intensity is raised to 1 amp. and 2 c.c. of lactic acid electrolysis being continued until the deposition of the zinc

n if all the zinc is deposited, a few drops of the electrolyte nd treated with a drop of potassium ferrocyanide: no tur- be produced, even after some time. Another method con- ting to the upper extremity of the stem of the cathode, by nding screw, a stout copper wire previously cleansed by a n in nitric acid, and bending this wire twice at right angles into the electrolyte for a few centimetres without touching if the wire does not show a faint bluish deposit of zinc after the deposition is complete. The electrolytic beaker is then small beaker filled with distilled water, the cathode being some time, washed with water, alcohol and ether and dried

*Estimation with rotating electrodes.* The ammoniacal solution is sulphuric acid, rendered alkaline with sodium hydroxide y acid by means of 25% formic acid solution; the liquid is 0° and electrolysed: coppered Winkler cathode<sup>3</sup>; rotating rotations, 1000 per minute; temperature, 40-50°; ND<sub>100</sub>

much ferric hydroxide, it is advisable to precipitate twice to get rid of

5. **Determination of the Phosphorus.**—See Analysis of Phosphor Bronzes.

6. **Determination of the Arsenic, Sulphur and Bismuth.**—The methods given for the analysis of copper (*q.v.*) are followed.

## B. Gravimetric Methods

In a small covered beaker, 0.5 gram of the sample is dissolved in 15 c.c. of nitric acid (D 1.2) at a gentle heat.

1. **Determination of the Tin.**—When the action is complete the solution is diluted with 15–20 c.c. of water and, if it appears turbid on account of the presence of metastannic acid, evaporated to dryness. The residue is heated for some time with a few drops of nitric acid and a little water, and the metastannic acid filtered off, washed with hot water acidified with nitric acid, ignited and weighed :  $\text{SnO}_2 \times 0.7881 = \text{Sn}$ .

2. **Determination of the Lead.**—The liquid freed from the metastannic acid, or the original solution if the alloy does not contain tin, is diluted with 3–4 c.c. of concentrated sulphuric acid, evaporated to dryness and heated on a sand-bath until white fumes of sulphuric acid appear. On cooling, the residue is taken up in 50 c.c. of water, gently heated and filtered to dissolve the basic copper and zinc sulphates, allowed to cool and diluted with 15 c.c. of 95% alcohol. After standing for 1–2 hours, the lead sulphate separated is collected on a Gooch crucible, washed first with a mixture of 60 c.c. of water, 10 c.c. of alcohol and 0.5 c.c. of sulphuric acid and then with alcohol until the filtrate is neutral ; the crucible is then dried in an air-oven in a roomy porcelain crucible :  $\text{PbSO}_4 \times 0.6831 = \text{Pb}$ .

3. **Determination of the Copper.**—The filtrate from the lead sulphate is evaporated until the alcohol is completely expelled, the residue is heated to boiling with 100 c.c. of water and the copper precipitated with hydrogen sulphide. The liquid is decanted on to a filter and the precipitate washed first with saturated hydrogen sulphide solution containing 20 c.c. of 2N-sulphuric acid in 100 c.c. and afterwards with saturated hydrogen sulphide solution alone ; the precipitate is dried and the copper determined as cuprous sulphide :  $\text{Cu}_2\text{S} \times 0.7986 = \text{Cu}$ .

4. **Determination of the Iron.**—The filtrate is freed from hydrogen sulphide, concentrated to a small volume, treated with a few drops of hydrogen peroxide to oxidise the iron, boiled and rendered alkaline with dilute ammonia. After a short rest on the water-bath, the precipitated ferric hydroxide is filtered, washed, ignited and weighed :  $\text{Fe}_2\text{O}_3 \times 0.7023 = \text{Fe}$ . If the amount of ferric hydroxide is considerable, the precipitate is

of sulphur :  $\text{ZnS} \times 0.6709 = \text{Zn}$ .

**Ammoniation of the Nickel.**—The filtrate from the zinc precipitate to expel hydrogen sulphide, concentrated, rendered faintly ammoniacal, and the nickel precipitated with alcoholic dimethylglyoxime (*see* Analysis of Nickel Steel and of Argentan).

**Ammoniation of the Arsenic, Sulphur and Bismuth.**—The methods for the analysis of copper (*q.v.*) are followed.

**Ammoniation of the Phosphorus.**—*See* Analysis of Phosphorus.

\* \* \*

Many brassy brasses, besides copper and zinc, often contain small quantities of iron (sometimes up to 1%), in some cases tin (0.5–1%) and antimony (0.5–1%) and, in general, the impurities present in the copper and zinc used in the preparation.

A good brass should exhibit a fracture of uniform colour and fine and homogeneous texture. It should not contain more than 0.01% of antimony, as otherwise it is brittle and unfit for hammering; it should not contain more than 0.05% of arsenic.

The following table gives the percentage compositions of some of the commoner commercial brasses:

TABLE XXII  
Composition of Brasses

Variety.	Cu	Zn
Commercial brass, Mannheim gold (for cheap jewellery)	85–95	5–15
Brass for sheets and plates . . . . .	60–72	28–40
Brass for bolts . . . . .	65–70	30–35
Brass for rivets . . . . .	66–67	33–34
Brass for wire . . . . .	60–67	33–40
Brass (Fontainmoreau bronzes) . . . . .	1–10	90–99 <sup>1</sup>
Brass for welding . . . . .	34–90	10–66 <sup>2</sup>

## SPECIAL BRASSES

In the following table are indicated those alloys of copper and zinc which contain small quantities of one or more other elements (especially lead, tin, antimony, manganese, aluminium) introduced for the purpose of imparting special properties. The most important are as follows,

<sup>1</sup> Often contains 1–2% of lead.

<sup>2</sup> Sometimes contains also small quantities of tin.

Lead brasses are very soft and therefore suitable for casting worked at the lathe. Their analysis comprises, besides determining copper and zinc, also that of lead and of the impurities usually occurring in ordinary brass (iron, tin, nickel, sulphur, phosphorus, arsenic, bismuth, etc.). The analytical methods are exactly those used for ordinary brass (*q.v.*).

\* \* \*

Lead brasses usually contain 1-3% of lead and such impurities as are found in common brass.

## Tin Brasses

Tin brasses are used especially for making tubes, plates, valves, etc., for naval construction. They are analysed by the same methods as ordinary brass (*q.v.*).

\* \* \*

Tin brasses contain on the average 60-62% Cu, 37.5-39% Zn and 1-2% Sn. In this category fall *Naval brass*, *Iron brass* and *Laveyssière brass*.

## Manganese Brasses

Manganese is introduced in small quantities into brass to increase its strength, elasticity and hardness. The constituents of these brasses are determined as with the complex brasses (*see later*).

\* \* \*

The two types in most common use have the compositions: (1) 59-60-41% Zn, traces of Mn, and (2) 58-59% Cu, 39-40% Zn, 1.8-2.2% Mn. They are used in marine construction, especially for making propellers.

The following table gives the compositions prescribed for manganese brasses by the American Society for the Testing of Materials and by the Technical Committee for Steam Plant of the United States Navy (*Industria*, 1914):

TABLE XXIII  
Compositions of Manganese Brasses

	Cu	Zn	Sn (max.)	Fe (max.)	Al (max.)	Mn (max.)

\* \*

brasses in more common use have the following mean compositions :

*metal* : 55-60% Cu, 38-42% Zn, 1.5-2% Fe, 0-0.8% Sn.

*metal* : 58-60% Cu, 36-41% Zn, 0.7-1.8% Fe, 0-1% Sn.

## Aluminium Brasses

Aluminium brasses have properties similar to those of manganese and iron and find the same uses in naval construction. They are analysed in the same ways as the other brasses (*q.v.*).

\* \*

Aluminium brasses in more common use have the following mean compositions (Guillet) :

(1) Copper, 68-70 ; zinc, 31-27 ; aluminium, 3-1.

(2) „ 64-66 ; „ 33-30 ; „ 4-1.

(3) „ 58-61 ; „ 40.5-37.5 ; „ 1.5-3.

## COMPLEX BRASSES

Complex brasses have properties very similar to those of manganese brasses and are largely used, particularly for making propellers, anchors, gun tubes, etc.

Complex brasses may contain at the same time : iron and manganese ; aluminium ; iron, manganese, aluminium and, sometimes, tin. The analysis includes determinations of the components proper (Cu, Zn, Fe, Sn) and of any extraneous elements present as impurities (Pb, Ni, etc.), and may be carried out electrolytically or by a combined gravimetric and volumetric method.

### A. Electrolytic Method<sup>1</sup>

In a covered beaker, 1 gram of the sample is dissolved in 10-12 ml. of 10% nitric acid (D 1.2) at a gentle heat.

**Determination of the Tin.**—The solution is diluted with 15-20 ml. of water and, if turbid owing to the presence of metastannic acid, filtered on a dryness, the residue being taken up with a few drops of nitric acid and a little water. The liquid is heated for some time and the metastannic acid filtered off, washed with hot water acidified with nitric acid, and dried. Weighed :  $\text{SnO}_2 \times 0.7881 = \text{Sn}$ .

which separates is collected in a Gooch crucible and is washed first with water, then with alcohol, and finally with ether. The residue is dried in a vacuum desiccator and weighed:  $\text{PbSO}_4 \times 0.6831 = \text{Pb}$ .

**3. Determination of the Copper.**—The filtrate is evaporated to dryness to eliminate the alcohol, the residue being diluted with water to 150 c.c. and electrolysed at the ordinary temperature. Cathode, platinum foil; anode, spiral;  $\text{ND}_{100} = 0.1-0.2$  amp.; voltage, 1.7-2.0 volts; time, 15-16 hours.

During the whole course of the electrolysis, the voltage at the cathode should never exceed 2, so that it is advisable to use a single accumulator or a battery of accumulators joined in parallel. At the completion of the copper deposition, the electrolytic beaker is lowered slowly and the electrodes washed as they emerge. The washing of the cathode is complete with water, alcohol and ether, and the weight determined after drying.

**4. Separation of the Iron and Manganese.**—The spiral anode, which is covered with a black coating of manganese dioxide, is immersed in the liquid from which the copper has been separated, this being done with addition of 3-4 drops of hydrogen peroxide until the manganese dioxide is completely dissolved. The spiral is withdrawn and washed, and the solution concentrated to 30-40 c.c. and poured, little by little and with shaking, into a solution of 10 grams of pure sodium hydroxide in 30 c.c. of water contained in a platinum or porcelain dish. The iron and manganese are precipitated as oxides, while the zinc and aluminium precipitate as sodium zincate and aluminate. The liquid is heated to boiling, diluted with boiling water and filtered, the filtrate being collected in a half-litre beaker containing about 100 c.c. of 20% sulphuric acid and the residue washed with hot water. The oxides separated are dissolved in dilute sulphuric acid containing a few drops of hydrogen peroxide and the solution again poured into sodium hydroxide solution of the concentration mentioned above, the latter being heated to boiling, diluted and filtered, and the filtrate collected in the same half-litre beaker as the other filtrate.

(a) DETERMINATION OF THE IRON. The ferric and manganese hydroxides are redissolved in the least possible quantity of 10% sulphuric acid, 10 drops of hydrogen peroxide being added and the solution heated to boiling. The greater part of the free acid is neutralised with ammonia and the solution is poured into a boiling solution of 6-7 grams of ammonium oxalate in 100 c.c. of water; after addition of 5-6 c.c. of 2% hydrazine sulphate solution, the solution is diluted to about 200 c.c., the liquid is electrolysed to determine the iron (see Ferro-manganese, Electrolytic Analysis).

the manganese determined as indicated in the electrolytic analysis of manganese.

**Determination of the Zinc.**—If not already acid, the solution of the zinc and aluminium is acidified with dilute sulphuric acid, and if necessary to reduce the volume to 200–250 c.c., rendered alkaline with sodium hydroxide, acidified slightly with formic acid and analysed with rotating electrodes to determine the zinc (*see* p. 225).

**Determination of the Aluminium.**—The liquid from which the copper has been removed, together with wash water, is treated with ammonium hydroxide and ammonia until the reaction is alkaline, boiled for some time, the aluminium hydroxide filtered off, washed, dried, ignited and weighed.  $\frac{W}{0.5303} = \text{Al.}$

**Determination of the Phosphorus, Sulphur, Bismuth, Arsenic, and Ordinary Brass.**

## Combined Gravimetric and Volumetric Method

10 g. of the sample are dissolved in 20 c.c. of nitric acid (D 1.2) at 50°C.

**Determination of the Tin, Lead and Copper.**—The liquid is diluted with 15–20 c.c. of water, and the tin, lead and copper determined gravimetrically as in ordinary brass (*q.v.*).

**Determination of the Iron, Manganese, Zinc and Aluminium.**—The liquid from which the copper has been separated as sulphide is reduced to reduce its volume to about 200 c.c. and to expel the hydrogen, the iron being oxidised by addition of a few drops of hydrogen peroxide. The cooled liquid made up to 300 c.c.

**GRAVIMETRIC DETERMINATION OF THE IRON.** The iron in 50 c.c. of the solution is reduced with zinc amalgam and titrated with permanganate in the usual way.

**GRAVIMETRIC DETERMINATION OF THE MANGANESE.** Two other portions of 50 c.c., are used for the determination of the manganese gravimetrically (method (*see* Ferro-manganese), one for the preliminary test and the other for the actual determination.

**GRAVIMETRIC DETERMINATION OF THE ZINC.** A further quantity of 50 c.c. is rendered alkaline with ammonia and then neutralised with formic acid; 10 c.c. of this solution 4 c.c. of 50% formic acid are added and precipitated by hydrogen sulphide. The liquid is left overnight for complete precipitation and is then filtered through a filter-paper of Whatman No. 541 and washed with a dilute solution of ammonium formate.



(d) DETERMINATION OF THE ALUMINIUM. The liquid from which zinc has been removed is concentrated in a porcelain dish to small volume, the iron being then oxidised with hydrogen peroxide and the solution rendered alkaline with pure potassium hydroxide solution, boiled, with boiling water and filtered. The filter is washed with hot water, the filtrate acidified with nitric acid, rendered alkaline with ammonium hydroxide, heated to boiling for a short time. The precipitated aluminium hydroxide is filtered off, washed, dried to some extent, ignited in a platinum crucible and weighed:  $\text{Al}_2\text{O}_3 \times 0.5303 = \text{Al}$ .

**3. Determination of the Phosphorus, Sulphur, Arsenic, Bismuth, etc.**—See Ordinary Brasses.

\* \* \*

Of these complex brasses the one most largely used is the so-called "naval metal," of the following mean composition: 54-62% Cu, 38-40% Zn, 0.4-1.2% Fe, 0.02-2.5% Al, 0.0-0.5% Pb and 0-3% Sn.

## ORDINARY BRONZES

Analysis of ordinary bronzes includes, besides determinations of the constituent metals (copper, tin and sometimes zinc), also those of the extraneous metals often present in small quantities (lead, iron, antimony, nickel, manganese, phosphorus, arsenic, sulphur, etc.). Electrolytic and gravimetric methods may be used.

### A. Electrolytic Method

In a covered beaker, 1-3 grams of the alloy, as filings or turnings, are treated in the cold with 15-20 c.c. of nitric acid ( $D = 1.3$ ), the liquid is heated gently when the action slackens and finally evaporated almost to dryness.

**1. Determination of the Tin.**—The residue is taken up with 10 drops of nitric acid, 50 c.c. of water being mixed in and after about 10 minutes on the water-bath, the liquid filtered through a compact filter-paper. The residue on the filter washed with hot water acidified with nitric acid (1 of acid to 100 of water). The filtrate is utilised as described in § 3. The metastannic acid separated may be dried, ignited and weighed. The filtrate may contain various impurities (especially copper and phosphorus) when an exact analysis is required the following procedure is advised.

<sup>1</sup> The method of fusion with sulphur and sodium carbonate indicated for the gravimetric analysis of bronzes (see p. 234) may also be used and, when the anti-

10–15 c.c. of sodium sulphide solution (D 1·225) in a small water-bath until the metastannic acid is completely dissolved. Then with 10–15 c.c. of water and addition of a little sodium sulphide in a little water to reduce polysulphides, the liquid is again stirred for a short time and filtered by decantation, the filtrate being collected in a conical flask. The residue is again treated with 10–15 c.c. of sodium sulphide solution, heated, reduced with sulphite, diluted, filtered and washed with hot water containing a little sodium sulphide until about 100 c.c. of filtrate are collected. The lead, copper, iron, etc., contained in the filtrate and the metastannic acid remain on the filter as sulphides. The filter is then burnt in a small dish, the residue being dissolved in a little water (D 1·3) and the solution obtained added to the liquid in which the lead, zinc, etc., are to be determined.

For the determination of the tin and antimony, hydrochloric acid with an equal volume of water is added gradually and with stirring (under a draught hood) to the solution in sodium sulphide until it shows an acid reaction; 25–30 c.c. of concentrated hydrochloric acid are then added and the liquid boiled to dissolve the separated sulphur, if necessary, a few crystals of potassium chlorate.

When cooled, the solution—which contains sulphur and is turbid—is diluted with alkaline water with ammonia and then heated with 5 grams of oxalic acid until all the tin hydroxide precipitated by the addition of ammonia is dissolved. Then 7 grams of ammonium oxalate are added, the liquid heated and hydrogen sulphide passed for about 15 minutes through the liquid. Under these conditions, any antimony present is alone

allowed to cool somewhat in the current of hydrogen sulphide, then filtered, the filtrate being collected in a  $\frac{1}{2}$ -litre beaker and the residue washed with a hot 1% oxalic acid solution saturated with hydrogen sulphide. The antimony sulphide precipitate remaining on the filter is then treated according to 2 (below).

The filtrate is treated with 30 c.c. of conc. hydrochloric acid and 20 grams of ammonium oxalate, boiled for a short time to eliminate hydrogen sulphide, a few drops of hydrogen peroxide added, heated again for a short time, cooled to 40–50°, made up to about 300 cc and electrolysed, under a hood, to determine the tin : coppered Winkler cathode <sup>1</sup>; current, 1 amp.; ND<sub>100</sub> = 1 amp.; voltage = 3–4; temperature, 40–50°, time (with 0·1–0·3 gram Sn) 4–5 hours.

When the deposition of the tin is complete, the electrolytic beaker is removed without interrupting the current, by another full of water; after the cathode is detached, washed with an abundant supply of water

**2. Determination of the Antimony.**—The filter-paper with antimony sulphide is heated in a beaker with 4 c.c. of 50% sodium hydroxide solution and 20–30 c.c. of sodium sulphide ( $D = 1.225$ ) until the antimony sulphide is completely dissolved. After some time the liquid is poured directly into the Classen dish, the vessel and filter being washed with 10 c.c. of sodium sulphide. The filtrate is treated with 5–6 grams of potassium cyanide to decolorise the sodium sulphide and to prevent formation of polysulphides during the electrolysis, which is carried out at the ordinary temperature. Cathode, Classen capsule; anode, disc or spiral; current = 0.15–0.18 amp.; voltage = 1–1.2; duration (0.1–0.15 gram) 15–18 hours.

When the antimony is all deposited, the anode is withdrawn, the capsule rapidly emptied, washed with water, alcohol and ether, and dried at  $70^{\circ}$ .

The antimony is afterwards removed from the dish by treatment with nitric acid ( $D 1.2$ ) containing a little tartaric acid in solution.

**3. Determination of the Copper, Lead, Iron and Zinc.**—The residue from which the metastannic acid was separated (*see* 1) is acidified with 15–20 c.c. of nitric acid ( $D 1.2$ ), mixed with the nitric acid solution of the oxides extracted from the metastannic acid and the whole treated as usual in the analysis of ordinary brass (*q.v.*).

**4. Determination of the Nickel.**—*See* Nickel Bronzes.

**5. Determination of the Manganese.**—*See* Manganese Bronzes.

**6. Determination of the Silver.**—5–10 grams of the sample is treated with nitric acid and freed from metastannic acid in the ordinary way. In the filtrate the silver is precipitated with hydrochloric acid in the procedure followed for the determination of silver in copper.<sup>1</sup>

**7. Determination of the Phosphorus.**—*See* Phosphor Bronze.

**8. Determination of the Arsenic.**—*See* Copper.

**9. Determination of the Sulphur.**—2 grams of the sample is treated with nitric acid and the stannic acid separated as usual. In the filtrate the copper is eliminated by electrolysis in nitric acid solution, the residual liquid being evaporated to dryness and the sulphur then determined as in copper (*q.v.*).

## B. Gravimetric Method

**1. Determination of the Tin.**—In a covered beaker, 1–2 grams of the alloy as filings are treated with 15–20 c.c. of nitric acid ( $D 1.3$ ) until the solution is clear.

sodium sulphite until it becomes pale yellow.<sup>1</sup> The liquid is and, the precipitate washed with water containing a little sodium and then with hydrogen sulphide solution; the filter is burnt in and the residue dissolved in a little nitric acid and the solution the filtrate from the metastannic acid containing the bulk of the , zinc, etc., dealt with as in 3.

tion contains all the tin and antimony present as sulpho-salts. s treated in a  $\frac{3}{4}$ -litre conical flask with 6 grams of caustic potash, tartaric acid and, slowly and, if necessary, with cooling, with % hydrogen peroxide to give complete decoloration, that is, the sulphide completely into sulphate. The liquid is boiled ne to expel excess of hydrogen peroxide, allowed to cool, neu- fully with oxalic acid, treated with an excess of 3-5 grams of diluted to 250-300 c.c., heated to boiling, and a moderate current sulphide passed through the boiling liquid for about an hour. s then allowed to cool somewhat and any precipitated antimony lected in a tared Gooch crucible, and washed first with 1% solution saturated with hydrogen sulphide and afterwards with hot acetic acid saturated with hydrogen sulphide.

rmine the tin, the filtrate is rendered slightly alkaline with cidified with acetic acid, and the tin precipitated with hydrogen after the precipitation, the liquid is left at rest for about half the water-bath to facilitate the separation of the precipitate, filtered, being washed with hydrogen sulphide solution contain- mmonium sulphate in solution. The tin sulphide thus obtained 20°, converted by ignition into oxide and weighed.

**Determination of the Antimony.**—The antimony sulphide in the ble is converted by any of the known methods<sup>2</sup> into the tri- d weighed directly:  $\text{Sb}_2\text{S}_3 \times 0.7142 = \text{Sb}$ .

**Determination of the Lead, Copper, Iron, Zinc, etc.**—The ined after the action of nitric acid on the alloy, together with cid solution of the metals extracted from the metastannic acid, with 2-3 c.c. of conc. sulphuric acid, the further procedure being the analysis of ordinary brasses (*q.v.*).

**Determination of the Manganese, Silver, Phosphorus, Arsenic ur.**—See preceding method.

\* \*

positions of bronzes vary widely with the requirements as regards asticity, colour, sonority, etc.

for machine gearing and the old, highly elastic, tenacious and

As a rule commercial bronzes, besides copper and tin, contain small quantities of other elements (especially zinc, iron, manganese, nickel, lead, antimony, phosphorus, arsenic, sulphur, etc.), which, even in small proportions, markedly modify the properties of the alloy (*see* Special Bronzes); so much so that it is not always easy to decide if these elements are impurities in the raw materials used or if they have been added to obtain certain properties.

Zinc in small quantities (0.5–2%) renders bronze more easy to cast and increases its strength and elasticity; if, however, the proportion is greater than 2%, the bronze loses its hardness and strength and assumes properties approximating to those of the brasses.

The presence of lead is especially harmful in bronzes for machines and even if it is only slightly greater than 0.5%, since it diminishes the homogeneity of the alloy. In proportions not exceeding 1.5%, iron exerts an action analogous to that of zinc and increases considerably the hardness of the bronze. Antimony, bismuth and sulphur are highly injurious, and even in the proportion of 0.1% render the bronze brittle. Nickel, manganese and phosphorus improve the quality of the alloy and are often added (*see* Nickel-bronze, Manganese-bronze, Phosphor-bronze, etc.).

## SPECIAL BRONZES

These are copper-tin alloys containing another element added for a definite object. Those in more common use are: phosphor-, manganese-, lead-, nickel-, lead-nickel- and aluminium-bronzes.

### Phosphor-bronzes

Phosphor-bronzes are so called because during their preparation a definite quantity of phosphorus is added as phosphor-copper or phosphor-tin with a view to reduce the metallic oxides contained in the metal and, thereby, to impart greater hardness, strength, elasticity, etc. The attempt is usually made to add the quantity of phosphorus just necessary for the deoxidation (there may, therefore, be phosphor-bronzes free from phosphorus), but most only a slight excess, so that only a very small amount passes into the alloy. The analysis includes determinations of the usual constituents and impurities and also that of phosphorus.

**1. Determination of the Phosphorus.**—(a) IN ABSENCE OF ARSENIC. 2 grams of the sample are dissolved in aqua regia or in hydrofluoric acid and potassium chlorate, the solution being repeatedly evaporated to dryness with hydrochloric acid, the residue then dissolved in dilute hydrochloric acid and water and the phosphoric acid precipitated with ammonium molybdate as in the determination of phosphorus in iron (*see* p. 17).

(b) IN PRESENCE OF ARSENIC. After the repeated evaporations

mination of Tin, Copper, Zinc, etc.—See Ordinary Bronzes.<sup>1</sup>

\* \* \*

bronzes for bushes, pistons, etc., subject to attrition, quantities of varying from 0.25 to 2.5% are sometimes present with a view to give special effects. In ordinary phosphor-bronzes smaller quantities (less than 0.25%).

### Silicon-bronzes

are used especially for telegraph and telephone wires, as they have high electrical conductivity and resistance to tension. Their analysis

**Determination of Silicon.**—2–10 grams of the sample, according to the assumed silicon content, are treated with aqua regia (3 parts of hydrochloric acid and 1 part of nitric acid), the solution being evaporated to dryness, the residue taken up twice with about 15 c.c. of concentrated hydrochloric acid and evaporated, and the residue heated in an oven at 100°C. until the silica completely insoluble. The residue is treated with 10% hydrofluoric acid, the subsequent procedure being as in the determination of iron. In the present case also the purity of the silica must be ascertained by treatment with sulphuric and hydrofluoric acids.

**Determination of the Tin, Iron, Zinc, Nickel, Phosphorus, and Arsenic.**—As with ordinary bronzes<sup>2</sup> (*q.v.*).

\* \* \*

bronzes, besides a little tin and often a little zinc, contain very small quantities of silicon (0.05–1%) introduced in the form of silicon-copper as a hardener. According to Hampe the best bronzes for telegraph and telephone wires have the following percentage compositions :

TABLE XXIV

### Compositions of Silicon-bronzes

	Cu	Sn	Si	Fe	Zn
Telephone wires .	97.12	1.14	0.05	trace	1.12
Telegraph wires .	99.94	0.03	0.03	trace	—

### Lead-bronzes

bronzes, also called American bronzes owing to their widespread use in America, besides copper and tin contain considerable quantities of lead, and sometimes small quantities of zinc, phosphorus, and

solved in dilute hydrochloric acid and the filtrate (400-500 c.c.) and the solution treated with hydrogen sulphide. The precipitate is washed in a Gooch crucible with hot water saturated with hydrogen sulphide, acidified with hydrochloric acid and the filtrate evaporated to dryness with nitric acid.

The residue is dissolved in a little nitric acid and the phosphoric acid precipitated with ammonium molybdate as in the determination of phosphorus in iron.

\* \* \*

The following table gives the compositions of various types of common lead-bronzes (Guillet, Muspratt, Ledebur) :

TABLE XXV  
Composition of Lead-bronzes

	Cu	Sn	Pb	Zn	P	Fe	Sb	Ni
1 . . .	84.70	10.05	4.60	0.46	0.11	—	0.14	—
2 . . .	84.00	3.00	4.56	8.50	—	—	—	—
3 . . .	83.85	8.32	7.36	0.13	0.31	trace	—	—
4 <sup>1</sup> . . .	79.70	10.00	9.50	—	0.80	—	—	—
5 . . .	73.50	9.50	9.50	9.50	—	0.50	—	—
6 . . .	78.01	10.36	10.45	—	0.57	0.09	—	0.26

### Manganese-bronzes

Manganese-bronzes, which should not be confused with manganese-brasses—often improperly given this name—or manganese-copper alloys are composed essentially of copper and tin with small proportions of manganese (1-3%). Their analysis comprises :

**1. Determination of the Tin.**—As in ordinary bronzes.

**2. Determination of the Lead, Copper, Iron, Manganese and Zinc.**—The liquid from which the metastannic acid has been separated together with the solution of the metals occluded in the metastannic acid is evaporated with sulphuric acid and the separate determinations carried out as with complex brasses.

**3. Determination of the Phosphorus, Arsenic and Sulphur in Ordinary Bronzes.**

<sup>1</sup> Type adopted by the Italian State Railways.

92	8	—	1	—
84	14	—	2	—
82	15	—	3	—
92	8	3	0.5	trace

## Nickel-bronzes

tion of small proportions of nickel to bronzes increases the lustre and imparts a pleasing, golden colour.

alysis includes :

**mination of the Tin.**—2 grams of the sample are treated, tall, narrow beaker with 20 c.c. of nitric acid (D 1.2), the g evaporated to dryness, taken up with a few drops of nitric water and heated for a short time on the water-bath. The acid is collected on a close filter-paper and, being in small y be weighed directly after washing with hot water acidified acid, drying and calcining.

**mination of the Lead, Copper, Iron, Nickel and Zinc.**—ts are determined in the liquid freed from metastannic acid ods given for the analysis of argentan (*see later*).

**mination of the Phosphorus, Arsenic and Sulphur.**—*See* onzes.

\* \* \*

onzes have the following mean composition : 88-89% Cu, 2-3% , 2-3% Ni, and 0.1-0.3% Pb.

## Lead-nickel-bronzes

very soft and are also called plastic bronzes and serve mostly n metals. Their analysis comprises :

**mination of the Tin.**—2 grams of the alloy are dissolved tall, narrow beaker with 20 c.c. of nitric acid (D 1.3), the solu- ted to dryness, and the analysis continued as with ordinary ).

**mination of the Lead.**—The solution freed from metastannic solution of the oxides of copper and lead retained by the meta- are evaporated together to a small volume and then heated



given for the gravimetric analysis of ordinary brasses.

**3. Determination of the Copper, Iron, Nickel and Zinc ELECTROLYTICALLY.** The liquid freed from lead is evaporated until alcohol is expelled and the residual liquid mixed with 20 c.c. of nitric acid and electrolysed as in the case of argenta.

(b) **GRAVIMETRICALLY.** The liquid freed from lead is evaporated to eliminate the alcohol, mixed with 200–250 c.c. of water, heated to boiling and the copper precipitated with hydrogen sulphide, the subsequent procedure being that described for the gravimetric analysis of argenta.

**4. Determination of the Phosphorus, Arsenic and Sulphur.**  
*See* Ordinary Bronzes.

\*  
\* \*

Lead-nickel-bronzes have the following mean composition : 64% Cu, 24% Pb, 5% Sn, and 1% Ni.

## Aluminium-bronzes

Aluminium-bronzes have a fine, golden-yellow colour and are used for making vases, ornamental articles, etc. They consist essentially of copper and aluminium (3–10%) and often contain small quantities of silicon and iron. Their analysis includes :

**1. Determination of the Silicon.**—1 gram of the alloy is dissolved gently with 10 c.c. of nitric acid (D 1.2) and the solution evaporated to dryness. The residue is mixed with 10 c.c. of 50% sulphuric acid until white fumes of sulphuric acid appear. The residual liquid is mixed with 30 c.c. of water, heated for some time to boiling, when cold, filtered through a small filter ; the residue of more or less silica is washed, dried, calcined in a platinum crucible and weighed. The filtrate is then treated with hydrofluoric acid, etc., as in the determination of silicon in iron.

**2. Determination of the Copper.**—The filtrate is treated with 10 c.c. of nitric acid, diluted to about 150 c.c. and subjected to electrolysis (see Electrolytic Determination of Copper in Ordinary Brasses).

**3. Determination of the Iron and Aluminium.**—After removal of the copper, the liquid is rendered alkaline with ammonia, boiled for some time and the precipitated aluminium and ferric hydroxides filtered, washed, calcined and weighed. The oxides are then fused with potassium bisulphate, the residue taken up in dilute sulphuric acid and the iron and aluminium determined electrolytically or volumetrically. The iron and aluminium are thus obtained separately.

biles)	. . .	94.9	4.7	0.41	0.10
	. . .	95.4	4.0	0.33	0.12
	. . .	97.0	2.7	0.19	0.20

---

## ZINC AND ITS ALLOYS

place zinc as such will be treated and methods described for its common impurities ; technical tests for zinc dust are also regards the numerous alloys in which zinc occurs, those with salt with under copper and its alloys and those with nickel under s alloys.

## ZINC

neous elements commonly found in commercial zinc are lead, mium. Small quantities of arsenic, antimony and sulphur found and in remelted zinc also tin, but only rarely are traces icon, phosphorus, copper, nickel, cobalt, etc., found.

tial determinations to be made on commercial zinc are those and cadmium. It may sometimes be of interest to estimate ntimony and sulphur, but as a rule it is sufficient to test quali- he other elements.

**nination of the Lead, Iron and Cadmium** (according to romm <sup>1</sup>).—To 100 grams of the sample and 200 c.c. of water, ding about 2 litres, nitric acid is added gradually until, with g, the metal is completely attacked.

ion obtained is then treated with ammonia until the zinc first separating redissolves, and then diluted to about two litres, mmonium sulphide being next added in small quantities and until the lead, iron and cadmium are completely precipitated hide begins to appear.<sup>2</sup> The liquid is kept at 80° for a short ate separation of the precipitate, which consists of lead, cad- ., sulphides mixed with zinc sulphide, and is filtered off when nt solution becomes clear. The precipitate is treated on the t, dilute hydrochloric acid,<sup>3</sup> which dissolves lead, cadmium

*Anal. Chem.*, 1897, p. 37.

ortion of the liquid, filtered and treated with ammonium sulphide, should ly white precipitate.

chloric acid (20 c.c. of conc. HCl made up to 100 c.c.). It is advisable l in a wash-bottle and to wash with it also the flask in which the precipi- ce. About 150–200 c.c.<sup>4</sup> to be used in all.

(b) DETERMINATION OF THE CADMIUM. The liquid freed from sulphate is evaporated until the alcohol is expelled, neutralised with ammonia, treated for every 100 c.c. of liquid with 10 c.c. hydrochloric acid (D 1.125) and then with hydrogen sulphide. The precipitate is filtered off, washed with saturated hydrogen sulphide solution and dissolved in nitric acid (D 1.2), the solution being evaporated in a tared platinum crucible in presence of a slight excess of sulphur, the excess of the latter being eliminated and the residue heated gently and weighed:  $\text{CdSO}_4 \times 0.5392 = \text{Cd}$ .

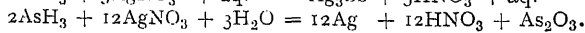
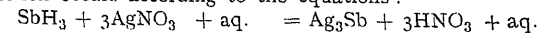
(c) DETERMINATION OF THE IRON. The excess of hydrogen sulphide is eliminated from the filtrate from the cadmium sulphide, the iron is oxidised by a few drops of hydrogen peroxide or bromine water, and ammonia is added until the reaction is alkaline. After a short rest on a water-bath the precipitated ferric hydroxide is filtered and washed. To free the precipitate from all traces of zinc, it is redissolved in dilute hydrochloric acid, again precipitated with ammonia, filtered off, washed with slightly acidulated water, dried, ignited and weighed:  $\text{Fe}_2\text{O}_3 \times 0.6994 = \text{Fe}$ .

**2. Determination of the Sulphur, Antimony and Arsenic** (according to Gunther<sup>1</sup>).—100 grams of the sample are placed in a large flask furnished with a delivery tube and with a tapped funnel, the neck of which, bent up at the end, reaches almost to the bottom of the vessel. The air is expelled by means of pure hydrogen washed by passing it through a silver nitrate solution and the delivery tube connected with two washing bottles, the first containing a solution of cadmium cyanide in potassium cyanide and the second silver nitrate solution, pure dilute sulphuric acid being then gradually introduced by means of the tapped funnel until the metal dissolves completely. When evolution of gas ceases, a moderate current of hydrogen is passed through the apparatus to displace the products of the reaction. The first washing bottle retains the sulphuric acid and cadmium sulphide, which is filtered off and converted into sulphate and weighed.

In the second bottle, if hydrogen arsenide and antimonide are present, metallic silver and silver antimonide<sup>2</sup> separate. The precipitate is filtered off, washed and dissolved in nitric and tartaric acids, the silver being precipitated as chloride, which is filtered off, washed, dried and weighed. In the filtrate, the greater part of the acidity is neutralised with a

<sup>1</sup> *Zeitschr. analyt. Chem.*, 1881, XX, p. 503.

<sup>2</sup> The reaction occurs according to the equations:



oxide. The silver corresponding with the amount of antimony (Ag,Sb) is deducted from the total silver found, and the arsenic combined with the remainder calculated:  $2\text{As} = 12\text{Ag}$ .

\*  
\* \*

zinc of good quality should not contain more than 1.5% of elements (Pb, Fe, Cd, Cu, etc.) and not more than 0.1% of As, Sb and

The presence of lead in small quantities (0.2–1.5%) in zinc is not harmful, but with more than 2–3% of lead, zinc becomes brittle and difficult to roll into sheets. Iron rarely occurs in greater proportion than 0.2% amount is not injurious, but in greater quantity it renders the metal brittle. Cadmium also is always present in small proportion (0.01–0.05%) not deleterious unless the zinc is to be used for making zinc white. Arsenic, antimony and sulphur are usually present in small quantities, but if together they exceed 0.1% the metal is very brittle; a small amount of carbon is exerted by copper to the extent of 0.5%. Carbon and silicon, sometimes be present in small proportions, have no appreciable effect.

Compositions of various refined zincs of commerce are as follows (Schnabel, 1904; Hollard) :

TABLE XXVIII

### Composition of Zincs

	Zn <sup>1</sup>	Pb	Fe	Cd	Ag	Cu	Sb	As	S	Si	C
...	98.782	1.118	0.024	0.012	—	—	0.022	—	—	—	—
...	98.930	1.000	0.030	0.018	—	—	—	—	—	—	—
Ortho	99.981	—	0.019	—	—	—	—	—	—	—	—
d'Art	98.904	1.070	0.016	0.010	—	—	—	—	—	—	—
...	99.757	0.192	0.049	trace	—	0.002	—	—	—	—	—
...	98.752	1.1524	0.0073	0.0705	0.0002	trace	0.0020	0.0015	0.0035	0.0025	0.0075
...	99.868	0.1094	0.0065	0.0075	trace	0.0005	0.0018	0.0005	0.0005	0.0035	0.0006

## ZINC DUST

Commercial zinc dust constitutes a mixture of very finely divided zinc and zinc oxide and variable proportions of cadmium, iron, lead, antimony, etc., and is used as a reducing agent. It is usual to determine the reducing power towards solutions of potassium dichromate or potassium permanganate; in some cases, however, the volume of hydrogen obtained from the reaction of dilute hydrochloric acid is measured, the quantity of zinc present being deduced therefrom.

**Determination of the Reducing Power.**—*Reagents:* N/2-potas-

is continued for 10-15 minutes—until all the zinc is dissolved. The is emptied and washed into a half-litre measuring flask and made volume. 100 c.c. of the solution are acidified with 5 c.c. of hydrochloric acid ( $D = 1.10$ ) and treated with 10 c.c. of 10% potassium iodide solution, the iodine separated being titrated with sodium thiosulphate and starch paste. The difference in c.c. between the volumes of dichromate and thiosulphate, multiplied by 0.01635, gives the amount of zinc in gram of the sample.

\*  
\* \*  
\*

Commercial zinc dust contains 80-90% Zn, 9-10% ZnO, 1.5-2% Pb, small quantities of copper, cadmium, arsenic, antimony, iron, sulphur, carbon, etc., and, sometimes, of calcium and magnesium oxides.

## LEAD AND ITS ALLOYS

Lead is largely used as such and also enters into the composition of numerous alloys.

Methods will be given here for the analysis of commercial lead and hard lead, alloys of lead with tin and antimony (solder, white antiferrous metal, white metal for fittings, etc.) being treated under tin and its alloys.

### LEAD

The analysis of commercial lead consists in determining the impurities present (silver, copper, bismuth, cadmium, arsenic, antimony, iron, nickel, cobalt, zinc and manganese). These impurities are, however, present in very small proportions (refined lead contains, indeed, 99.96-99.99% lead) and it is therefore necessary to employ large quantities of the sample in order to conduct all the analytical operations with the greatest precision.

In a 1.5-litre beaker, 200 grams of the metal are gently heated with a mixture of 500 c.c. of nitric acid ( $D 1.2$ ) and 500 c.c. of water. After standing for about 12 hours, the liquid is filtered, the insoluble residue (lead antimonate) being collected on a small filter, washed, placed in a porcelain crucible and kept apart (residue *a*).

The filtrate is treated with 62-63 c.c. of concentrated sulphuric acid and left to cool and settle, the clear supernatant liquid being siphoned into a 3-litre beaker. The residue is shaken with 200 c.c. of water acidified with nitric acid, allowed to settle and the supernatant liquid added to the first solution; to ensure complete washing, this operation should be repeated three or four times.

filtrate is added to the alkaline sulphide solution and the solution is evaporated to dryness and treated at the boiling point with sodium carbonate for the determination of the *antimony* and *arsenic* (*see* 3) ; on the other impurities remain as sulphides.

The precipitate thus obtained is dissolved in nitric acid (1 vol. of nitric acid, 2, and 2 vols. of water) and the liquid evaporated with a slight excess of sulphuric acid to eliminate the small quantities of lead still present in the nitric acid (excess of sulphuric acid is necessary to keep lead in solution) ; the residue is taken up in a little water, filtered and precipitated with hydrogen sulphide. *Bismuth, silver, cadmium* and *copper* are precipitated (*see* 1), whilst *nickel, cobalt, iron, zinc* and *manganese* remain in solution (*see* 2).

**DETERMINATION OF THE BISMUTH, SILVER, CADMIUM AND COPPER.** The sulphides precipitated with hydrogen sulphide are dissolved in nitric acid and the solution evaporated in presence of sulphuric acid.

**DETERMINATION OF THE BISMUTH.** The residue is dissolved in a little water, almost neutralised with pure sodium hydroxide, treated with sodium carbonate in slight excess and with a little potassium cyanide and evaporated. If bismuth is present, a white precipitate is obtained, this is filtered off, well washed and dissolved in a little nitric acid. The solution is then precipitated with a slight excess of ammonia, the precipitate is filtered, washed and dissolved in nitric acid and the solution evaporated to dryness in a porcelain crucible ; the residue is ignited gently and weighed :  $0.965 = \text{Bi}$ .

**DETERMINATION OF THE SILVER.<sup>1</sup>** The filtrate from the treatment with sodium carbonate and potassium cyanide is treated with a little more potassium cyanide and a few drops of sodium sulphide, the silver and cadmium are precipitated as sulphides, while any copper present remains in solution.

The precipitate is collected, washed, dissolved in nitric acid and the silver is reprecipitated as chloride by addition of a few drops of dilute nitric acid :  $\text{AgCl} \times 0.7526 = \text{Ag}$ .

**DETERMINATION OF THE CADMIUM.** The filtrate from the silver determination is evaporated almost to dryness and treated at the boiling point with sodium carbonate. The precipitate formed is collected, washed with water and dissolved in a little nitric acid, evaporated in a tared porcelain crucible, gently ignited and weighed :  $\text{CdO} \times 0.8754 = \text{Cd}$ .

**DETERMINATION OF THE COPPER.** The filtrate from the silver and cadmium determinations (*see* b) is treated with a little sulphuric and nitric acids and a few drops of hydrochloric acid and evaporated to dryness. The residue is dissolved in water and the copper determined electrolytically or gravimetrically.

The silver is more exactly determined directly by cupellation (*see* Silver and its

with a mixture of 5 parts of saturated hydrogen sulphide solution and 1 part of hydrochloric acid (D 1.2). The iron, zinc and manganese sulphides are dissolved and these metals are determined as in (b) and (c); and cobalt sulphides remain on the filter and are determined as in (a).

(a) DETERMINATION OF THE NICKEL AND COBALT. The nickel and cobalt sulphides, which have remained undissolved, are ignited and weighed as oxides, which are then dissolved in aqua regia, the solution rendered alkaline with ammonia, and the nickel precipitated with dimethylglyoxime (see Argentan).

(b) DETERMINATION OF THE IRON. The hydrogen sulphide is expelled by boiling from the hydrochloric acid solution containing the iron, zinc and manganese, oxidation being effected by a few drops of nitric acid, the liquid made alkaline with ammonia. The precipitated ferric hydroxide is collected, washed and dissolved in hydrochloric acid, the iron being reprecipitated with ammonia and weighed as ferric oxide:  $\text{Fe}_2\text{O}_3 \times 0.7000 = \text{Fe}$ .

(c) DETERMINATION OF THE ZINC. The filtrates from the iron precipitation are together rendered alkaline with ammonia and treated in a flask with 2-3 c.c. of ammonium sulphide, the flask being then filled with water, stoppered and left for 24 hours. The zinc and manganese sulphides are then collected, washed and treated on the filter with dilute acetic acid, which dissolves only the manganese sulphide. The residue, consisting of zinc sulphide, is dissolved on the filter by dilute hydrochloric acid and the solution evaporated to dryness in a tared crucible. The residue is mixed with an aqueous suspension of a little pure mercuric oxide free from arsenic, evaporated to dryness, heated gently over a naked flame to eliminate the mercury, ignited over a blowpipe flame and weighed:  $\text{ZnO} \times 0.8034 = \text{Zn}$ .

(d) DETERMINATION OF THE MANGANESE. The acetic acid solution containing the manganese is concentrated and treated with ammonia and hydrogen peroxide to precipitate the manganese, the precipitate being collected, washed, dried, ignited and weighed:  $\text{Mn}_3\text{O}_4 \times 0.7203 = \text{Mn}$ .

**3. Determination of the Arsenic and Antimony.**—(a) DETERMINATION OF THE ARSENIC. The alkaline sulphide solution obtained as described on p. 245 is acidified with acetic acid and heated for 3-4 hours on the water-bath, the arsenic and antimony sulphides and sulphur being separate being filtered off. The precipitate is washed with saturated hydrogen sulphide solution slightly acidified with acetic acid, dried, freed from sulphur by means of carbon disulphide, filtered, and the arsenic and antimony sulphides dissolved in hydrochloric acid and potassium chlorate. The liquid is filtered through a small filter, and the filtrate treated

ammonium arsenate is collected on a filter, transformed into pyroarsenate and weighed:  $\text{Mg}_2\text{As}_2\text{O}_7 \times 0.4827 = \text{As}$ .

TERMINATION OF THE ANTIMONY. The filtrate from the ammonium arsenate is treated with ammonium sulphide and acidified with sulphuric acid. The antimony is thus precipitated as sulphide, dissolved in ammonium sulphide, the solution being evaporated in a porcelain crucible, oxidised with nitric acid, calcined gently and weighed:  $\text{Sb}_2\text{O}_4 \times 0.7898 = \text{Sb}$ .

\*  
\* \*

Commercial lead of commerce, especially that destined for making electrical plates, is a very pure metal, containing 99.96–99.99% Pb.

Analyses and compositions of samples of lead of different origins are as follows (Hollard, Hampe):

TABLE XXIX

### Composition of Samples of Lead

	Pb	Sb	Ag	Cu	Zn	Fe	Bi	As	Cd	Ni	Mn
Lead	99.9915	0.0050	0.001	0.0003	0.0006	0.0016	—	—	—	—	—
Lead	99.9937	0.0013	0.0006	—	0.00085	0.0014	0.0021	—	—	—	—
Lead	99.99	0.0030	0.0010	0.0005	0.0021	0.0047	0.0007	—	—	—	—
Lead	99.9924	0.0012	0.0002	0.0002	0.0007	0.0017	0.0030	—	—	—	0.0002
Lead	99.9852	0.0044	0.0006	0.0007	0.0005	0.0011	0.0073	—	trace	trace	—
					Zn, Ni, Co						
Lead	99.989	0.003	—	trace	0.005	0.012	0.091	—	—	—	—
Lead	99.9575	0.0040	trace	0.0018	0.0002	0.0015	0.0350	trace	trace	—	—

### HARD LEAD

Hard lead or antimonial lead is an alloy of lead and antimony containing small quantities of copper and tin and sometimes also iron, nickel, arsenic, etc., and serves for making type, the plates of certain electric accumulators and cast ornamental articles, and as anti-rattle, etc.

Essential determinations to be made on these alloys for a complete analysis (see Table B) are those of the lead, antimony, copper and tin, determinations of iron, nickel, arsenic, etc., not being always necessary. Often, for the determination of certain elements only are required (see Partial



**2. Direct Determination of the Tin.**—From 2 to 4 grams sample in fine filings are heated to boiling, in an inclined long-necked covered with a funnel, with 20 c.c. of conc. sulphuric acid until the sulphate separating appears perfectly white. The cold mass is treated with 2–3 grams of tartaric acid dissolved in a little water and the solution introduced quantitatively into a 100 c.c. measuring flask, made up to volume, mixed and filtered through a dry, pleated filter. 50 c.c. of the filtrate are rendered alkaline with ammonia, heated gently with 5 grams of oxalic acid and the clear solution treated with 5 grams of ammonium oxalate, diluted to about 150 c.c. and kept gently *boiling* during the passage of hydrogen sulphide to precipitate the antimony and copper. After standing an hour, the liquid is allowed to cool a little and filtered, 1% oxalic acid solution saturated with hydrogen sulphide being used for washing.

The filtrate is boiled for a short time with 30 c.c. of hydrochloric acid and 20 grams of ammonium oxalate to expel the hydrogen sulphide. After being allowed to cool somewhat, the liquid is treated with a few drops of hydrogen peroxide, heated a short time, made up to about 300 c.c., cooled to 50–60° and electrolysed—turbid with sulphur as it often is—to determine the tin: coppered Winkler cathode, spiral Winkler anode, current = 1 amp., temperature about 50°, duration (0.1–0.3 gram Sn) 4–5 hours.

Since the antimony and copper sulphides precipitated may retain small amounts of tin, for an exact analysis the precipitation should be repeated twice. These sulphides are, therefore, dissolved in the hot in a mixture of 10–15 c.c. of conc. hydrochloric acid, 10–15 c.c. of 10% ammonium chloride solution and a few crystals of potassium chlorate, the solution being diluted with a little water, filtered, rendered alkaline with ammonia and treated with 5 grams of oxalic acid and 5 grams of ammonium oxalate, diluted to 100 c.c. and subjected at the boiling point to a current of hydrogen sulphide. After about an hour, the liquid is filtered and the precipitate washed with the oxalic solution saturated with hydrogen sulphide. The two filtrates are united and the solution—concentrated if necessary—of which an aliquot part of it used for the electrolytic determination of the tin.

### B. Complete Analysis

In a 250 c.c. measuring flask, 2.5 grams of the sample in fine filings are gently heated with 15 c.c. of water and 10 grams of powdered tartaric acid until the latter dissolves, 4–5 c.c. of nitric acid being added gradually.

cooled in a desiccator and weighed :  $\text{PbSO}_4 \times 0.6831 = \text{Pb}$ .

**Termination of the Antimony.**—The 50 c.c. of solution taken added to 20–30 c.c., neutralised with 50% sodium hydroxide excess of 3–4 c.c. of the latter and 30 c.c. of sodium sulphide (1.225) added and the liquid heated and, after some time, filtered the copper sulphide, etc., directly into a tared Classen capsule ; filtrate is washed with hot water in which a little sodium sulphide

The filtrate is treated with 50 c.c. of sodium sulphide and of pure potassium cyanide, mixed and electrolysed to determine antimony,  $\text{ND}_{100} = 0.15\text{--}0.18$  amp., voltage = 1–1.2, duration (0.1–0.2) 15–18 hours. When the deposition is complete, the capsule is thoroughly washed with water, alcohol and ether, dried at 70° C.

**Termination of the Tin and Copper.**—The 100 c.c. of solution rendered slightly alkaline with ammonia, treated with 5 grams of ammonium oxalate, heated to obtain a clear solution, treated with 7 grams of ammonium oxalate, and kept boiling for about an hour while a stream of hydrogen sulphide is passed to precipitate the antimony and copper. When the solution has cooled somewhat in the current of hydrogen sulphide, it is poured into a half-litre beaker, the filter being washed with a hot 1% oxalic acid solution saturated with hydrogen sulphide.

**TERMINATION OF THE TIN.** The filtrate is treated with 30 c.c. of hydrochloric acid and 20 grams of ammonium oxalate and boiled for some time to expel hydrogen sulphide. After the liquid has cooled a few drops of 30% hydrogen peroxide are added and the solution stirred for a little while, made up to 300 c.c., cooled to 40–45° and—added with sulphur—electrolysed to determine the tin : coppered cathode, spiral anode,  $\text{ND}_{100} = 1$  amp., voltage = 3–4, temperature 50°, duration (0.1–0.3 gram Sn) = 4–5 hours (*see also* Electrodeposition of Tin in Ordinary Bronzes).

**TERMINATION OF THE COPPER.** The precipitated copper and antimony sulphides, which have been filtered off, are heated gently with 10% sodium hydroxide solution and filtered, the filter being thoroughly washed with water faintly alkaline with sodium hydroxide ; the copper remains undissolved. The filter-paper and precipitate are dried at 100° C., the filter incinerated, the residue dissolved in nitric acid, the copper determined in this solution by the usual method (*see* Determination of Copper in Ordinary Brass).<sup>1</sup>

**Termination of the Iron, Nickel and Zinc.**—5 grams of sample are treated with nitric acid ( $D = 1.2$ ), the solution being left to stand in a water-bath for a short time and then filtered ; the filtrate is treated

Hard lead contains variable quantities of antimony (usually 10%) and may contain small amounts of copper, tin, iron, nickel, arsenic, etc.

The following table contains the results of analysis of samples of hard lead obtained directly, from ores of lead and antimony (Schnabel) :

TABLE XXX

## Composition of Hard Leads

Source.		Pb	Sb	Cu	As
Oberharz	I . . . .	81.71	17.69	0.62	—
	II . . . .	82.44	16.90	0.68	—
	III . . . .	82.08	17.34	0.62	—
Freiberg	. . . . .	—	15	—	2.5

## ANTIMONY AND ITS ALLOYS

Owing to its brittleness, antimony is rarely used as such, but it is a part of many industrial alloys, such as white bearing metals, type metal, etc.

Methods for determining the impurities commonly accompanying commercial antimony are therefore described, since the value depends on purity.

Lead-antimony alloys are treated under lead, while alloys of antimony with tin alone or with tin and lead together (white metals) are dealt with under tin.

## ANTIMONY

Analysis of commercial antimony is generally limited to the detection of its commoner impurities : lead, bismuth, copper, iron, arsenic, sulphur.

10 grams of the finely powdered sample are treated with aqua regia (140 c.c. HCl, 20 c.c. HNO<sub>3</sub>) diluted with an equal volume of water. The solution thus obtained being treated with 60-70 c.c. of 50% tartaric acid solution, then made alkaline with concentrated sodium hydroxide solution and subjected to a current of hydrogen sulphide. The separation of antimony sulphides is facilitated by heating on a water-bath, the precipitate

determination of lead in ordinary brasses (*see* p. 220).  
**Determination of the Bismuth.**—The liquid freed from lead is heated to expel the alcohol and treated with hydrogen sulphide to precipitate the bismuth and the copper. The precipitate is filtered off, washed with a hydrogen sulphide solution acidified with a few drops of sulphuric acid and dissolved in a little nitric acid (D 1·2). The solution is then treated in presence of sulphuric acid, taken up in a little water, neutralized almost completely with sodium hydroxide, and heated gently with an excess of sodium carbonate and a little potassium cyanide. The precipitate thus obtained is collected on a filter, washed, dissolved in nitric acid and again precipitated with ammonia under the conditions indicated for the determination of bismuth in lead.

**Determination of the Copper.**—The filtrate from the bismuth—precipitation is treated with sodium carbonate and potassium cyanide (*see* 2)—neutralized with nitric acid and a few drops of sulphuric acid, evaporated to dryness, taken up in hot water and the copper in the solution determined by the usual methods.

**Determination of the Iron.**—The filtrate obtained after removal of lead, bismuth and copper as sulphides (*see* 2) contains all the iron, which is precipitated by expelling the excess of hydrogen sulphide, oxidising with nitric acid and precipitating with ammonium chloride and ammonia.

**Determination of the Arsenic.**—*See* Determination of Arsenic in

**Determination of the Sulphur** (Hollard and Bertiaux).—5 g of sample are treated with nitric acid to which sufficient hydrochloric acid is added to give a clear solution. The liquid is evaporated to dryness, taken up again in nitric acid and evaporated several times with an excess of hydrochloric acid to expel the hydrochloric acid completely. The residue is finally dissolved in water faintly acidified with nitric acid and the solution filtered. The residue is washed with water. To the filtrate sufficient ammonia is added to redissolve the antimony oxide at first separating, excess of ammonia being then added and the liquid filtered. In the clear solution the sulphuric acid, formed by oxidation of the sulphur in the sample, is determined by means of barium nitrate.

\*  
\* \*

Commercial antimony generally contains small quantities of lead, copper, iron, and, sometimes, bismuth, nickel and cobalt. Pure antimony is a brittle metal, but the commercial metal has a slightly bluish tint owing to the presence of lead. It exhibits a marked tendency to crystallise and, indeed, a well-defined crystalline structure, which is manifested even on the outside by the surface resembling fern leaves, these being regarded—not always with

TABLE XXXI

## Results of Analyses of Antimony

Origin.	Sb	Cu	Fe	Pb	As	Bi	S
Hungary (Liptau) . .	98.27	0.54	0.63	—	—	0.36	—
California { I . . .	98.34	0.021	0.144	0.410	1.008	—	0.064
II . . .	99.081	0.052	0.039	0.538	0.036	—	0.254
Of various origins } I	98.98	0.01	0.35	0.34	0.09	—	0.23
(analysis by Hilmy) } II	98.87	0.02	0.16	0.73	0.09	—	0.11

## TIN AND ITS ALLOYS

Tin is one of the most important metals, being largely used as such also as a constituent of numerous industrial alloys.

Methods will be given here for the determination of elements occurring in commercial tin as impurities, for the analysis of tin-plate and the important tin alloys (phosphor-tin, solder, white antifriction metal, metal and metal for fittings).

Alloys of tin with copper (bronzes) are considered along with

## TIN

Commercial tin is usually contaminated by small quantities of copper, iron, bismuth, antimony, sulphur, and arsenic and sometimes of molybdenum, tungsten, zinc, manganese, nickel, chromium, etc. The more important determinations are those of lead, bismuth, copper, antimony, arsenic and sulphur, qualitative tests for the other elements being sufficient.

## 1. Determination of the Lead, Bismuth, Copper and Iron

According to the greater or less degree of impurity, from 10 to 20 g. of the sample, flattened on an anvil or in a small rolling mill and finely divided, are heated gently on a water-bath with aqua regia (1 vol. of aqua regia with 5 vols. of hydrochloric acid; 10 grams of the sample require 10 c.c., and 20 grams, 180 c.c.). When the metal is completely attacked, the liquid is allowed to cool and treated, according to the weight of sample taken, with 25–35 grams of tartaric acid; the latter is dissolved by

in Ordinary Brass).

**DETERMINATION OF THE BISMUTH AND COPPER.** The alcohol is in the liquid separated from the first lead sulphate precipitate. Bismuth and copper precipitated with hydrogen sulphide and as in the analysis of antimony.

**DETERMINATION OF THE IRON.** The iron is determined as oxide free from the bismuth and copper sulphides (*see* Determination of Antimony).

**Determination of the Antimony.**—10 grams of the sample are dissolved in 100 c.c. of hydrochloric acid (D 1.124) and potassium chlorate, after being eliminated by boiling, the volume made up to about 250 c.c., the liquid is heated on the water-bath, 6 grams of pure reduced iron in small quantities to displace the copper and antimony. The iron is removed with the small amount of undissolved iron, washed off and washed on the filter with dilute hydrochloric acid until it no longer gives the reaction for tin with mercuric chloride. The iron and antimony are then dissolved in hydrochloric acid and potassium chlorate, excess of chlorine expelled by boiling, the copper and antimony precipitated with hydrogen sulphide and the precipitate well washed and dissolved in 30 c.c. of sodium sulphide solution (D 1.225) to dissolve the antimony sulphide. The liquid is filtered directly into the Classen dish, washed with 50 c.c. of the sodium sulphide solution, and the filtrate, after addition of 5-6 grams of potassium cyanide, electrolysed to determine antimony (*see* Determination of Antimony in Hard Lead).

**Determination of the Arsenic.**—(a) 10 grams of the sample are dissolved in a solution of 100 grams of ferric chloride in 100 c.c. of water, 10 c.c. hydrochloric acid being added and the arsenic distilled in water (*see* Determination of Arsenic in Iron).

(b) 10 grams of the sample are dissolved in hydrochloric acid containing potassium chlorate, the chlorine being expelled by boiling, and the solution mixed with one-third of its volume of conc. hydrochloric acid and hydrogen sulphide passed through it for some hours. The arsenic precipitated is filtered off on an asbestos filter (Gooch crucible), washed with conc. hydrochloric acid and then with boiled water and ammonia; the solution is evaporated in a dish and the residue dissolved in conc. nitric acid, made strongly alkaline with ammonia and reprecipitated with magnesia mixture and alcohol. The precipitate is washed, transformed into pyroarsenate and weighed.

**Determination of the Sulphur.**—*See* Determination of Sulphur in

together, or more than 0.01% of bismuth, or more than 1% of total iron.  
The compositions of tins of different origin are as follows (Hollard, Sch

TABLE XXXII  
Composition of Samples of Tin

Source.	Sn	Pb	Fe	Cu	Bi	Sb
Straits Settlements { Banka . . . . .	99.961	0.014	0.019	0.006	—	—
Malacca . . . . .	99.805	—	0.020	0.072	—	0.060
Pulo Brani . . . . .	99.76	0.02	0.14	—	—	0.07
China (Hong-Kong) . . . . .	98.928	0.833	0.037	0.040	—	0.044
England . . . . .	99.76	—	trace	0.24	—	—
Germany { I . . . . .	99.336	—	—	0.480	0.060	0.545
II . . . . .	99.594	—	trace	0.406	—	—

## TIN-PLATE

With commercial tin-plate the most important determination made is that of the tin, the thickness of the layer of this metal determining the value; next comes the determination of the lead, which gives indication of the quality of the tin used. For these two determinations

Sometimes, however, for certain purposes (hygienic, for instance) the determination of the lead alone is of interest, it being desired to ascertain whether tinning has been done with commercial tin or with an alloy of lead and tin. The determination of the lead alone is described in 2.

**1. Determination of the Tin and Lead.**—From 1 to 2 sq. cm. of the tin-plate<sup>1</sup>—taken from the middle of the plate, since the tin-plate is often irregular at the edges—is measured exactly, de-fatted with benzene and weighed, so that the results may be referred to the weight as well as the surface of the sample. The measured portion is cut into small squares of 1–2 cm. side, these being heated to boiling for 5 minutes in a covered beaker with 50 c.c. of 10% hydrochloric acid (25–30 c.c. of concentrated hydrochloric acid diluted to 100 c.c. with water). The hydrochloric solution is decanted into a 300 c.c. measuring flask and the metal is treated for 5 minutes with another 50 c.c. of the acid, this being decanted off; if necessary, the residue treated a third time; the colour of the metal should be a uniform iron-grey when all the tin is dissolved. Tin and lead are easily dissolved in the hot by hydrochloric acid of this concentration, the iron is attacked but little.<sup>2</sup> The acid solution is then diluted with water

tin-plate electrodes. 100 c.c. of the filtrate are treated in a beaker with 20-30 c.c. of 40% sodium sulphite solution to polysulphides, made up to about 200 c.c. and electrolysed at 1000 amp. and then tinned Winkler cathode<sup>2</sup>; spiral anode, 1000 amp. minute; temperature, 60°; ND<sub>100</sub>, 3-3.5 amp.; voltage, 5-6; 5-20 minutes.

When electrolysis is complete, the rotation of the anode is suspended without interrupting the current, the electrolytic beaker replaced with water; after some time, the cathode is detached, washed with water, alcohol and ether, dried at 70° and weighed. The weight, multiplied by 3, gives the tin contained in the sample taken. When rotating electrodes are used, the determination of tin in tin-plate takes longer than an hour.

**Ordinary electrodes.** In a  $\frac{1}{2}$ -litre conical flask, 100 c.c. of the sulphide filtrate are treated, under a draught hood, with a little potassium cyanide to reduce the polysulphides, and hydrochloric acid and an equal volume of water added until the reaction is acid, the flask kept covered with a funnel and shaken meanwhile. When evolution of gas ceases, the liquid is boiled for some time with 25 c.c. of hydrochloric acid to dissolve the tin sulphide which separates and leaves the sulphur. After addition of 25 grams of ammonium oxalate to 250 c.c., the liquid is electrolysed: coppered Winkler cathode; spiral anode; ND<sub>100</sub> = 1 amp.; voltage = 3-4; temperature, 60°; time (for 0.1-0.5 gram Sn), 4-5 hours (*see also* Electrolytic Determination of Tin in Ordinary Bronzes). Multiplication by three of the tin weight gives the amount in the sample taken.

**Stannous chloride method.** In a  $\frac{1}{2}$ -litre conical flask, 50 or 100 c.c. of the alkaline filtrate (*see* 1, p. 254) are diluted with water and acetic acid added until the reaction is faintly acid, the tin being thus precipitated as sulphide. After standing overnight, the precipitate is filtered off, washed with 10% sodium acetate solution and dried at 100-120°. The filter and precipitate are weighed, placed in a tared porcelain crucible, the filter-paper incinerated and a few crystals of ammonium carbonate and then ignited. The stannous sulphide is completely converted into the white oxide of tin:  $\text{SnO}_2 \times 0.7881 = \text{Sn}$ .

In the absence of copper it is convenient to use sodium sulphide, but in such case the determination of the tin with rotating electrodes cannot be carried out.

**Coppering of the electrode, *see* p. 225.** For the subsequent tinning, the electrolytic solution is employed: 3-4 grams of stannous ammonium chloride are dissolved in 100 c.c. of cold water to which are added 150 c.c. of saturated ammonium bioxalate solution. The cathode is immersed in this solution and the current passed for some time. ND<sub>100</sub> = 0.2-0.5 ampere.



nium or sodium sulphide, and the filter and precipitate heated to with 15-20 c.c. of nitric acid (D 1.2) in a small covered beaker. The is decanted through a filter and the residue boiled with 20-30 c.c. following mixture, which dissolves also any small amount of lead s formed by oxidation of the sulphide: 40 c.c. of ammonia (D 0.923), of nitric acid (D 1.332) and 5 grams of copper nitrate. The liquid is the filter washed with hot water acidified with nitric acid, and the made up to about 200 c.c. and electrolysed to determine the lead: cathode; matte gauze cylinder anode; ND = 0.3 amp.; voltage (see also Electrolytic Determination of Lead in Ordinary Brass).

When the deposition of the lead is complete, the anode is washed with water alone, dried at 200-220° and weighed:  $\text{PbO}_2 \times 0.866 = \text{Pb}$ .

2. *Gravimetrically.* The lead and iron sulphides (see 1, p. 255) filter are well washed with water containing a little ammonium sulphate dissolved in nitric acid (D 1.2) and filtered by decantation. The is again boiled twice with nitric acid and finally washed with water acidified with nitric acid. The nitric acid solution is evaporated with sulphuric acid until white fumes appear, and the residue, when cold, taken up in water, the lead being determined as sulphate as in the case of tin.

**2. Determination of the Lead alone.**—The surface of the tin is scraped with a penknife so that as little as possible of the metal beneath is removed, about 1-1.5 gram of thin shavings being obtained. The particles of iron are removed with a magnet. The shavings are melted in a covered beaker with 6 c.c. of fuming nitric acid (D 1.5), 3 c.c. of water being poured carefully down the side of the beaker so that the two mix slowly and the action proceeds regularly. At the end of the reaction the liquid is heated to boiling, diluted with 50 c.c. of boiling water, when the liquid above the metastannic acid has become clear, filtered and decanted through a dense filter and washed by decantation with water slightly acidified with nitric acid.

In the filtrate the lead is determined either electrolytically or gravimetrically by the methods given for the analysis of alloys of lead and tin (see p. 259). When the lead is separated as peroxide or sulphate, tin unavoidably present is determined in the residual liquid by precipitation with ammonium chloride and ammonia. Deduction of the weight of tin found from the total weight of the shavings gives the amount of lead in the alloy taken for analysis, and to this the quantity of lead found is re-

bronzes, includes:

**Determination of the Phosphorus.**<sup>1</sup>—The alloy is treated with hydrochloric acid and the phosphorus thus liberated as hydrogen phosphide, oxidised with bromine water and determined as phosphoric acid. *Apparatus.* A flask of about 500 c.c. capacity furnished with a stopper through which pass (1) a tapped funnel for the introduction of the hydrochloric acid and (2) two tubes bent at right angles, one reaching almost to the bottom of the vessel and serving for the introduction of a stream of carbon dioxide into the apparatus, and the other to collect the gas evolved in the reaction. The latter tube communicates with three absorption bottles, the first containing bromine water and a small quantity of bromine (about 5 millimetres deep) and the third bromine water alone.

*Procedure.* 2–5 grams of the alloy in small fragments are introduced into the flask and the latter stoppered and connected with the washing apparatus, a current of carbon dioxide being passed for about five minutes to displace the air. From 50 to 100 c.c. of concentrated hydrochloric acid are added to the flask little by little, and when the attack is complete the liquid is allowed to boil, and a current of carbon dioxide again passed to drive off the phosphine products of the reaction. The contents of the three bottles are transferred to a beaker, the excess of bromine eliminated by boiling and the phosphine acid precipitated either (1) as magnesium ammonium phosphate by the addition of a solution of magnesium sulphate, standing, is filtered off, dried, ignited strongly and weighed:  $0.2787 = P$ ,<sup>2</sup> or (2) with ammonium molybdate (*see* Iron, 4).

**Determination of the Tin.**—The hydrochloric acid solution is transferred to a 500 c.c. measuring flask and made up to volume. An aliquot portion corresponding with 0.5–0.75 gram of the sample, is rendered alkaline with sodium hydroxide, the precipitate redissolved by addition of a little oxalic acid, the solution boiled for a short time with 25 c.c. of hydrochloric acid, 25 c.c. of ammonium oxalate and a few drops of hydrogen peroxide, made up to 250 c.c. and electrolysed at 40–50° to determine the tin (*see* Determination of Tin in Ordinary Bronzes).

\* \* \*

Phosphor-tin or tin phosphide usually contains about 4% of phosphorus. The brand marked N.o contains about 5% P and N.1, 2.5%. Other brands, however, contain only 1% or even less.

W. Mell and S. L. Archbutt, *Journ. Soc. Chem. Industry*, 1908, XXVII, p. 100.

If the sample contains arsenic, magnesium ammonium arsenate is precipitated with ammonium ammonium phosphate. In this case the weighed precipitate is dissolved in hydrochloric acid, the solution reduced with sulphur dioxide and the tin determined as before.

# ALLOYS OF LEAD AND TIN

The lead-tin alloys are used for *soldering* and for many other purposes such as making ornamental articles, statuettes, toys, tubes for paraffin perfumery, tin-foil, etc.

In these alloys, the essential determinations are those of the lead and tin (*see 1*). Sometimes, however, for special products, the determination of the lead alone or of the tin alone is of interest (*see 2*), whilst in other cases, determination of the impurities (Cu, Sb, As, etc.) is desired (*see 3*). (see Metals).

**1. Determination of the Lead and Tin.**—About 1 gram of the alloy as filings is treated in a covered beaker with 6 c.c. of fuming nitric acid ( $D = 1.5$ ) and 3 c.c. of water then poured carefully down the side of the beaker so that the two liquids mix slowly and the action proceeds quietly and regularly. When the action is complete, the liquid is heated to boiling, diluted with 50 c.c. of boiling water, and, when the liquid above the precipitated metastannic acid has become clear, filtered by decantation through a close filter-paper. The precipitate is washed by decantation with water slightly acidified with nitric acid, collected on the filter, washed with water<sup>1</sup> and treated as in *B*. The filtrate is utilised as in *A*.

## A. DETERMINATION OF THE LEAD.

1. *Electrolytically.* The filtrate is made up to volume and an aliquot part, containing about 0.2–0.25 gram of lead, is treated with 1–2 c.c. of pure copper dissolved in 10–15 c.c. of nitric acid, diluted to 200 c.c. and electrolysed at the ordinary temperature: Winkler anode; cyanide gauze cathode;  $ND_{100} = 0.3$  amp.; voltage = 2–2.2; and duration 1–2 hours.

When by raising the level of the liquid the deposition of the lead is to be complete—even although copper may still remain in solution—the electrolytic beaker is replaced by another filled with distilled water, the current being maintained. After some time the anode coated with lead peroxide is detached, washed with water *alone* and dried at 200–220°C. The factor for converting weight of peroxide into that of lead is 0.8635 or 0.8635 according as the amount of the peroxide is less than or between 0.1 and 0.3 gram, or above 0.3 gram (Classen).

2. *Gravimetrically.* The filtrate is evaporated in presence of 10 c.c. of conc. sulphuric acid until white fumes appear. When cold, the residue is taken up with 50 c.c. of water, heated gently and stirred, allowed to settle and treated with 15 c.c. of 95% alcohol. After 1–2 hours, the lead is collected in a Gooch crucible and weighed (*see Gravimetric Determination*).

and 10-15 c.c. of sodium sulphide (D 1.225), the remaining proceeding that given for the electrolytic determination of tin in ordinary (p. 232).

*symmetrically*. The filtered and washed metastannic acid precipitated at 100° and removed as far as possible from the filter to a tared crucible. The filter-paper is incinerated in a dish, the ash added to the precipitate, the whole moistened with a few drops of nitric acid, the acid evaporated and the residue ignited at first with an ordinary blowpipe afterwards by means of the blowpipe, and weighed <sup>1</sup>:  $\text{SnO}_2 \times 100$ .

### Determination of the Lead alone or of the Tin alone.

**TIN ALONE.** This is of interest in some tin-lead alloys composed of tin, such as solder for culinary utensils and the like.

A covered electrolytic beaker of 350 c.c. capacity, 1-3 grams of the alloy are treated, according to the amount of alloy taken, with 5-10 c.c. of fuming nitric acid (D 1.5), 3-9 c.c. of water being then allowed to run down the wall of the beaker. When the attack of the metal is complete, the liquid is boiled for a short time, diluted to about 250 c.c. with water, and thoroughly mixed with 2-3 grams of copper nitrate or with 1-1.5 gram of copper dissolved in a little nitric acid, the metastannic acid being allowed to settle and the liquid, *without filtering*, electrolysed to determine the tin. Winkler cathode; matte gauze cylinder anode;  $\text{ND}_{100}$ , 0.3 amp. for 2-2.2 hours. The cathode should touch the bottom of the beaker, the anode should not reach to within about 1 cm. from the layer of sediment (for the factor,  $\text{Pb} : \text{PbO}_2$ , see p. 258). In this way, even the small quantities of lead held by the metastannic acid may be liberated by electrolysis.

**LEAD ALONE.** In other types of alloy, consisting essentially of lead (e.g. hard lead) with small quantities of tin (0.5-15%), such as solder for tubes for perfumery, colours, etc., wires for electric valves, etc., it is of interest to determine the tin alone.

1-3 grams of the sample in filings or clippings are treated with 10-15 c.c. of boiling conc. sulphuric acid and, when the action is at an end, diluted somewhat. When the liquid is cold, 5-6 grams of tartaric acid are dissolved in it and the whole transferred to a 100 c.c. measuring cylinder, made up to volume, and filtered through a dry filter. The tin is determined in 50 c.c. of the filtrate in the way given for the determination of tin in hard lead (see p. 248).

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The composition of solder varies widely with the metals to be soldered and the nature of the flux used. The following are the compositions of some of the solders used in the manufacture of electrical apparatus.

to obtain the shining white colour of tin. With these last two types of tin-foil, the most important determination is that of the tin, this effected as for the tin alone in lead-tin alloys (*see* Alloys of Lead and Tin, p. 258). A complete analysis may be carried out by the method indicated for the analysis of lead-tin alloys, when these are the only constituent metals or by that given for white metal in the case of an alloy of lead, antimony and tin.

If the foil is tinned externally, the coating must be removed in such a way that the quantity of tin actually present in the alloy may be determined. If the foil is moderately thick, the surface layer may be removed mechanically from the two faces and the quantitative determination made on the sample thus prepared. If, however, the foil is too thin and weak to be scraped, the surface tin is removed by means of sodium hydroxide solution and hydrogen peroxide, which, at the proper concentration, easily attacks and dissolves the layer of tin, whereas the tin in the alloy is acted on very little or not at all or but slightly. The conditions to be observed are as follows.

From 5 to 6 grams of the foil are freed from grease by treatment with ether, cut into squares of about 1 cm. side and heated in a 200 c.c. flask with 20 c.c. of 10% sodium hydroxide to 40°, 6–8 drops of 30% (100 volumes) hydrogen peroxide being then added with continual shaking. The surface tin passes rapidly into solution and as soon as the lead-grey colour appears on the pieces of metal indicates that this process is complete, the alloy solution is decanted off and the residue washed repeatedly with water, alcohol and ether successively and dried at 60–70°. The foil being thus freed from the surface tin, the quantitative determination of the composition of the alloy is carried out by the methods indicated above.

## WHITE METAL

This includes many types of alloys with a basis of tin-antimony, lead-antimony or lead-tin-antimony, together with small quantities of copper and sometimes zinc and iron (rarely mercury and arsenic), used as anti-friction metals, type metal, metal for fittings, etc. The composition of these alloys therefore the analytical methods to be used, vary with the purpose for which the metal. Three groups may be distinguished:

- (1) *Alloys with a basis of tin* (70–85%) and *antimony* (10–15%), with a little copper (5–10%) and lead (0.5–2%), and perhaps zinc and iron.
- (2) *Alloys with a basis of lead* (60–80%), *antimony* (10–15%) and *tin* (10–25%), with a little copper (0.5–1%) and perhaps zinc, iron and antimony.
- (3) *Alloys with a basis of lead* (75–90%) and *antimony* (10–25%), with a little tin, copper, zinc, iron and antimony.

group the method of analysis will be described later, but for certain purposes only the content of copper or tin is of interest, a method is given which permits of the direct and moderately rapid estimation of each of these elements.

**Direct Determination of the Copper.**<sup>1</sup>—In a 200 c.c. measuring flask the alloy is heated gently with 20–25 c.c. of nitric acid when the action is complete, the nitrous vapours are eliminated by boiling and the liquid cooled, treated with 3 c.c. of conc. sulphuric acid, cooled, diluted somewhat, rendered alkaline with ammonia, added 15–20 c.c. of 10% sodium phosphate solution and made up to 200 c.c. and mixed. After standing, the liquid is filtered through a filter and 100 c.c. of the filtrate neutralised with nitric acid, treated with 10 c.c. of conc. nitric acid and 20 c.c. of 10% sulphuric acid, and electrolysed with a spiral Winkler cathode; spiral Winkler anode;  $ND_{100} = 0.2$  amp.; 8–2.2; and duration, 10–12 hours.

When the copper is completely deposited, the electrolytic beaker is removed and another small beaker full of distilled water acidified slightly with nitric acid, the cathode being detached after some time, washed with alcohol and ether, dried at 70° and weighed. (Weight of copper deposited = percentage of copper in the sample.)

If the alloy contains arsenic, the copper deposited may have a brown coating. In this case the deposit is dissolved in 5–6 c.c. of nitric acid and the solution diluted and again electrolysed.

**Direct Determination of the Tin.**—According to the supposed method, 1–3 grams of the alloy in fine filings are treated with 15–20 c.c. of concentrated, boiling sulphuric acid, the subsequent procedure being the same as for the direct determination of tin in hard lead (*see* p. 247).

## 1. Alloys with a Tin-Antimony Basis

These alloys usually contain 70–85% Sn, 10–15% Sb, 5–10% Cu, 0.5–1% Zn, and possibly zinc and iron. Their complete analysis is carried out

**Electrolytically.**<sup>2</sup>—In a conical flask covered with a small funnel, 10–15 grams of the alloy in turnings or filings is treated with the least possible quantity of aqua regia (10–15 c.c.). When the action is over, 10–15 c.c. of concentrated tartaric acid solution containing in solution 2–3 grams of tartaric acid are added and the solution made slightly alkaline with concentrated caustic soda solution. Then added with a further quantity of 2 grams of sodium hydroxide and 10 c.c. of sodium sulphide solution ( $D = 1.225$ ). The liquid is heated on

trolysed at the ordinary temperature to determine the antimony: Classen capsule cathode; disc or spiral anode;  $ND_{100} = 0.15-0.17$  amp.; voltage =  $1-1.2$ ; and duration =  $15-17$  hours.

When the whole of the antimony is deposited, the electrolyte is poured into a  $\frac{1}{2}$ -litre flask and the capsule and disc (or spiral) washed with a little water which is also poured into the flask. The capsule is then thoroughly washed with water, alcohol and ether, dried at  $70^\circ$  and weighed.

2. DETERMINATION OF THE TIN. The alkaline liquid freed from antimony is acidified faintly with dilute sulphuric acid (1 vol. acid, 2 vols. water), the flask being kept under a hood, covered with a funnel and shaken. The liquid is then boiled for some time to expel the bulk of the hydrogen sulphide and cyanogen compounds, left on a boiling water-bath for about 15 minutes and filtered through a filter-paper moistened with ammonium sulphate solution, the precipitate being washed with a little hot water saturated with hydrogen sulphide.

The filter and precipitate are then heated to boiling in a small covered beaker with 20 c.c. of conc. hydrochloric acid and 15-20 c.c. of 10% ammonium chloride solution, a few crystals of potassium chlorate being subsequently added to complete the action. The liquid is then diluted with 15-20 c.c. of boiling water, shaken and filtered into a  $\frac{1}{2}$ -litre flask, washing with hot water acidified with hydrochloric acid. The filtrate is rendered slightly alkaline with ammonia, treated with 5 grams of oxalic acid and heated a little, 5 grams of ammonium oxalate being added to the clear solution, which is then made up to 150-200 c.c. and subjected to a moderate current of hydrogen sulphide while gently boiling. Under these conditions the traces of copper dissolved in the sodium sulphide and also any arsenic present are precipitated. After about an hour the liquid is allowed to cool somewhat in the stream of hydrogen sulphide and is then filtered into a  $\frac{1}{2}$ -litre beaker and the filter washed with a hot 1% oxalic acid solution saturated with hydrogen sulphide. The filtrate is boiled with 25 c.c. of conc. hydrochloric acid and 12-14 grams of ammonium oxalate for about 15 minutes to expel the hydrogen sulphide, allowed to cool a little, treated with 3-4 drops of 30% hydrogen peroxide, boiled again, cooled to about  $50^\circ$  and, without removal of any suspended sulphur, electrolysed to determine the tin (*see* Electrolytic Determination of Tin in Ordinary Bronzes).

3. DETERMINATION OF THE COPPER AND LEAD. The filter and hydrogen sulphide precipitate (*see* 2) are incinerated in a small dish and then ignited, the residue being dissolved in 2-3 c.c. of nitric acid.

The sulphides remaining undissolved in the sodium sulphide (*see* A) are dissolved in 10-15 c.c. of boiling nitric acid (D 1.2), filtered by decantation, the residue being treated again twice with nitric acid and the united

upper have been separated is used for the determination of the copper as in ordinary brasses.

DETERMINATION OF THE ARSENIC. See Determination of Arsenic in

**Stannic acid.**—2 grams of the sample are acted on with a suitable quantity of aqua regia at a gentle heat on a water-bath. When the action is complete, the liquid is diluted with 10-15 c.c. of water and 3 grams of tartaric acid in solution, then rendered faintly alkaline with sodium hydroxide solution and treated with colourless sodium sulphide in very slight excess. The liquid is heated on a water-bath with stirring until the precipitate has settled and is then filtered by decantation. The hot water containing a little sodium sulphide being used for the filtrate, containing tin and antimony, is analysed according to the method for the precipitate, containing lead, copper, etc., according to 2.

DETERMINATION OF THE TIN AND ANTIMONY. The filtrate is made alkaline with sodium hydroxide and 200 c.c. treated in a  $\frac{1}{2}$ -litre flask with 6 grams of potassium dichromate, 6 grams of tartaric acid and slowly and, if necessary, with cooling, added 10% hydrogen peroxide to decolorise the solution, that is, to oxidise the sodium sulphide completely into sulphate. The liquid is then boiled for one time to expel excess of hydrogen peroxide, allowed to cool, and then treated with saturated oxalic acid solution and treated with 5 grams of tartaric acid, diluted to about 250 c.c. and subjected at the boiling point to a moderate current of hydrogen sulphide for about an hour. The solution is then allowed to cool somewhat in the stream of hydrogen sulphide. The antimony sulphide filtered off and washed with 1% oxalic acid solution and treated with hydrogen sulphide.

The antimony sulphide may contain small quantities of tin, it is treated with a mixture of 10-15 c.c. of conc. hydrochloric acid and 10-15 c.c. of ammonium chloride solution, a few crystals of potassium chlorate are added and when the mixture begins to boil. After dilution with water, the solution is filtered, made slightly alkaline with ammonia, treated with tartaric acid, diluted to 150 c.c. and the boiling liquid again treated with hydrogen sulphide. **FILTER**

**Determination of the tin.** The two filtrates are united, rendered alkaline with ammonia, acidified with acetic acid, and a current of hydrogen sulphide passed through the solution for about three hours. The solution is then boiled for about 30 minutes on a water-bath to facilitate the separation of the antimony sulphide, the latter is filtered off and washed with hydrogen sulphide solution. The tin sulphide thus obtained is dried at 120°, transformed by ignition into the oxide and the



inter (see 1) is dissolved in a little concentrated nitric acid; the solution is evaporated in a tared porcelain crucible, the residue treated carefully to avoid spurting, with nitric acid and the liquid evaporated to dryness. The treatment with nitric acid is repeated twice to ensure the complete oxidation of the sulphur, the residue being ignited and weighed:  $\text{Sb}_2\text{O}_3 \times 0.75 = \text{Sb}$ .

2. DETERMINATION OF THE LEAD, COPPER, IRON AND ZINC. The sulphides remaining undissolved in sodium sulphide are dissolved in concentrated nitric acid (D 1.2), the filtered solution treated with a little sulphuric acid and evaporated until white fumes appear, the subsequent procedure being as indicated for the gravimetric determination of lead, copper, iron and zinc in ordinary brass.

## 2. Alloys with a Lead-Antimony-Tin Basis

These alloys usually contain 60–80% Pb, 10–15% Sb, 10–25% Sn, a little copper and possibly zinc, iron, arsenic. The complete analysis is carried out as follows:

A. **Electrolytically.**—1 gram of the sample in fine filings is treated with 20 c.c. of conc. hydrochloric acid and 2–3 c.c. of conc. nitric acid, left overnight in order that the action may proceed slowly but completely.

1. DETERMINATION OF THE LEAD. The acid solution is treated with 10 vols. of absolute alcohol (220–230 c.c.), cooled and after a suitable time (3–4 hours)—when the bulk of the lead chloride has separated (only a few milligrams, to be estimated later, remain in solution)—filtered through a tared Gooch crucible, washed with alcohol to a neutral reaction, dried at 100° and weighed:  $\text{PbCl}_2 \times 0.7447 = \text{Pb}$ .

2. DETERMINATION OF THE TIN, ANTIMONY, COPPER, IRON AND ZINC. The alcoholic solution, freed from lead chloride, is evaporated to dryness, 5 grams of tartaric acid until the alcohol is completely expelled, then the residue made slightly alkaline with concentrated sodium hydroxide solution and then treated with 2 grams of sodium hydroxide and 15–20 c.c. of sodium sulphide solution (D = 1.225). After being heated for about 15 minutes on a water bath, the liquid is filtered into a Classen capsule, the precipitate washed five or six times with sodium sulphide solution (60–70 c.c.), the filtrate and then with hot water containing a few drops of sodium sulphide solution. The filtrate contains the tin and antimony and the insoluble residue the copper and traces of lead dissolved as chloride, and any iron and zinc present.

For the electrolytic determination of these elements, the method previously described (see 1, A, p. 261)<sup>1</sup> is followed.

B. **Gravimetrically.**

The solution is evaporated with 2-3 grams of tartaric acid until the residue is completely expelled, the residue being taken up in water and made faintly alkaline with concentrated sodium hydroxide solution. The liquid is treated with colourless sodium sulphide solution in very slight excess. The liquid is heated on the water-bath and filtered, the subsequent analysis being that for the gravimetric analysis of alloys with a tin-antimony containing a little copper (*see* p. 263).

### 3. Alloys with a Lead-Antimony Basis

These alloys usually contain 75-90% Pb, 10-25% Sb, and small quantities of tin and copper (0.5-2%). Their complete analysis is carried out by the methods given for hard lead.

\*  
\* \*

These metals vary in composition according to their uses, the analytical methods of some of the commoner types being as follows:

TABLE XXXIII

#### Composition of White Metal

Type.	Su	Pb	Sb	Cu	Fe	Zn
<i>Friction metals :</i>						
the Italian Railways .	83	—	11	6	—	—
French " .	83.33	—	11.11	5.55	—	—
Russian " .	90	—	8	2	—	—
German " .	78.5	—	11.5	10	—	—
Austrian " .	83	—	11	6	—	—
the bearing metal .	82	—	12	6	—	—
metal . . . . .	76.7	—	15.5	7.8	—	—
	90-92	—	8-9	up to 3	—	—
<i>and fittings metals :</i>						
the Italian Railways .	14	76	10	—	—	—
French Northern Railway .	12	73	15	—	—	—
French Eastern Railway .	12	80	8	—	—	—
certain German Railways .	42	42	16	—	—	—
metal . . . . .	15	68	17	—	—	—

## NICKEL AND ITS ALLOYS

Nickel is largely used for nickel plating and for coins of low value, and also occurs in many alloys.

Descriptions will be given here of the tests to be made on commercial nickel and of the analysis of german silver and the like, which are the most important nickel alloys. For the analysis of bronzes containing nickel, *see* Nickel-bronzes.

### NICKEL

The more common determinations involved in the analysis of commercial nickel are those of copper, cobalt, iron, manganese, carbon, sulphur, arsenic and silicon.

10 grams of the sample are dissolved in nitric acid and evaporated in presence of sulphuric acid until dense white fumes appear. When cold the residue is treated with water acidified with sulphuric acid, heated to boiling, filtered and washed with boiling water acidified with sulphuric acid. The residue on the filter is treated according to 1 and the filtrate as described in 2, 3 and 4.

**1. Determination of the Silicon.**—The insoluble residue, consisting of silica and possibly metastannic acid, graphitic carbon, etc., is dried, ignited in a platinum crucible, weighed, treated with hydrofluoric acid and a few drops of sulphuric acid, heated to expel excess of acid, again ignited, cooled and weighed. The loss in weight gives the silica and therefore the silicon (*see* Determination of the Silicon in Iron).

**2. Determination of the Copper.**—The copper is precipitated in the filtrate by means of hydrogen sulphide and is then determined either as oxide or electrolytically by dissolving the sulphide in nitric acid and electrolysis of the solution.

**3. Determination of the Nickel and Cobalt.**—(a) *Determination of the nickel.* The filtrate from the copper sulphide is made up to volume in a 500 c.c. measuring flask, and 100 c.c. (corresponding with 2 grams of the sample) evaporated to dryness. The residue is taken up in ammonia and the volume then made up to 100 c.c. with ammonia (D 0.91), 5 grams of ammonium sulphate being dissolved in the liquid and the latter electrolysed to determine the nickel and cobalt together: Winkler cathode; spiral Winkler anode;  $ND_{100} = 0.7-1$  amp.; temperature, ordinary, and duration, 15-17 hours.

in the same Retort apparatus with dilute sulphuric acid, the cobalt passes. The aqueous layer is separated—washing with dilute sulphuric acid—and evaporated to dryness, the residue taken up in a little water, the solution made faintly ammoniacal and the nickel present with the cobalt precipitated with alcoholic oxime solution. The precipitate is filtered off, the filtrate taken up in a small flask with nitric and sulphuric acids to destroy organic matter, the residual liquid placed in a tared crucible, where the excess of nitric acid is expelled and the remaining cobalt sulphate then weighed :  
 $0.4 = \text{Co}$ .

**Determination of the Iron and Manganese.**—The 400 c.c. of the filtrate (8 grams of the sample)—quite free from hydrogen sulphide—is taken up to about 1.5 litre, treated with hydrogen peroxide and made ammoniacal, heated and then left at rest for a short time on a water-bath, the supernatant liquid being subsequently siphoned off and the residue of iron and manganese oxides collected on a filter. The residue is dissolved in a little hydrochloric acid and the precipitation repeated with hydrogen peroxide and ammonia repeated, the precipitate being left on a short rest on the water-bath, washed with slightly ammoniacal water, dried, ignited and weighed.

The ferric and manganese oxides together. The iron alone determined either by titration or by separating it as basic acetate.

**Determination of the Carbon.**—3 grams of the sample are taken up in the water-bath in concentrated copper-potassium chloride solution, the carbonaceous residue being collected on an asbestos filter, washed and burnt in a current of oxygen (*see* Determination of Carbon, p. 68).

**Determination of the Sulphur.**—10 grams of the sample are taken up in nitric acids, evaporated several times with hydrochloric acid and taken up in water and hydrochloric acid and filtered. In the filtrate the sulphuric acid formed by oxidation of the sulphur is precipitated with barium chloride solution.

**Determination of the Arsenic.**—From 10 to 20 grams of the sample are dissolved in nitric acid, the solution evaporated with sulphuric acid, the nitric acid is completely expelled, the residue dissolved in water and taken up with 5–10 grams of ferrous sulphate and excess of hydrochloric acid, and the arsenic determined by distillation (*see* Determination of Arsenic, p. 100).

\* \* \*

The nickel is more or less pure according to the processes used to separate the impurities which it may contain (Cu, Co, Fe, Mn, Sn, Pb, Sb, Bi, As, etc.).

be used for preparing alloys, and nickel, which is always present in commercial nickel to the extent of 1-2%, copper, which does not exceed 1%, and the other elements mentioned above, provided these are present only in small proportions, have no deleterious effect on the technical properties of the metal.

The following table gives the properties of samples of nickel of different sources (Lunge, Hollard) :

TABLE XXXIV  
Results of Analyses of Nickel

Origin.	Ni	Co	Cu	Mn	Fe	Sb	As	Pb	S	C	Si	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO and Alkalies	P
German Cubes { I .	97.08	0.89	0.15	—	1.22	—	—	—	trace	0.02	—	0.35	0.12	trace	—
{ II .	98.21	1.19	0.07	—	0.25	—	—	—	trace	trace	—	0.24	trace	trace	—
Granules from "Königs- warter and Ebell" .	98.58	0.75	0.10	—	0.24	—	—	—	trace	trace	0.26	—	trace	trace	—
English cubes . . .	96.86	1.26	0.06	—	1.05	—	—	0.40	trace	0.09	—	0.10	trace	trace	—
"Landore" cylinders .	97.48	1.05	0.06	—	0.79	—	—	—	trace	trace	—	0.38	0.22	trace	—
Unknown origin { I .	95.17	1.71	1.13	0.91	0.58	—	trace	—	trace	0.22	—	0.16	0.03	trace	—
{ II .	92.58	0.94	3.77	1.49	0.31	0.04	trace	—	trace	0.18	—	0.39	0.14	trace	0.05
French coinage <sup>1</sup> .	97.75	1.587	0.102	—	0.259	—	—	—	0.039	—	—	0.254	—	—	—
Electrolytic nickel .	99.22	0.71	0.01	0.046	—	—	0.006	—	—	—	—	—	—	—	—

## GERMAN SILVER

### (Argentan, Packfong, Alfénide)

Owing to their colour and stability, these alloys are used for domestic articles, for ornaments in place of silver, for coinage, etc. They all consist essentially of copper, nickel and zinc, sometimes with small quantities of lead and iron and, in rare cases, tin and manganese. Other alloys of similar appearance, used for coating rifle bullets or for coinage, consist of 70-80% Cu, 20-30% Ni, and small proportions of lead, iron, zinc, etc.

The analysis of german silver and of copper-nickel alloys in general is carried out as follows :

#### A. Electrolytically <sup>2</sup>

In a small covered beaker, 0.5 gram of the alloy is gently heated on a water-bath with 15 c.c. of nitric acid (D 1.2), the solution being subsequently diluted with 20-30 c.c. of water. Turbidity indicates tin, which is determined as in 1; a perfectly clear liquid is, however, used at once for the determination of copper and lead (*see* 2).

**1. Determination of the Tin.**—The liquid is evaporated to dryness, the residue taken up in a little water and a few drops of nitric acid and the

tion is at once diluted to about 150 c.c. and electrolysed for the electrolytic determination of the copper and lead (*see* Electrolytic Determination of the Copper and Lead in Ordinary Brasses, p. 224).

After the alloy contains tin and the solution is evaporated to separate the metastannic acid, the filtrate is treated with 15 c.c. of 10% (D 1·2), diluted to 150 c.c. and electrolysed.

**Determination of the Iron.**—The liquid from which the copper has been separated, together with the wash water from the first separation, is evaporated until white fumes of sulphuric acid appear, in order to convert the nickel and zinc nitrates into sulphates; the 10% sulphuric acid added to the electrolyte is sufficient for this purpose. When the residue is taken up with water acidified with sulphuric acid and placed in a water-bath, the clear solution being treated with a few drops of hydrogen peroxide and made alkaline with ammonia. After a short time in a water-bath, the precipitate is filtered off, dried, ignited and weighed.  $\text{Fe}_2\text{O}_3 \times 0.6994 = \text{Fe}$ .

**Determination of the Nickel.**—The filtrate from the ferric hydroxide is made up to about 150 c.c. and then mixed with 30 c.c. of concentrated ammonia and 0.1 gram of hydroxylamine sulphate, the electrodes are inserted but the circuit not closed. A thermometer is fitted and the beaker covered with the two halves of a clock-glass having gaps for the electrodes and for the thermometer and heated to 90°. A few drops of fresh concentrated sodium sulphite solution are then added and the electrolysis immediately started, the temperature being kept at 90° and occasional small quantities of ammonia (1 vol. conc. to 1 vol. water) added from a wash-bottle to replace that lost by heating: Winkler cathode; spiral Winkler anode,  $\text{ND}_{100} = 10$ ; voltage = 2; temperature = 90°; duration (0.1 gram Ni) = 100 s.

The liquid changes from blue to colourless, a drop of it is withdrawn and treated with alcoholic dimethylglyoxime solution to ascertain whether the nickel is completely deposited. When this is the case, the flame is tested with the thermometer taken out and washed, the cover removed and the electrolytic beaker replaced by another filled with distilled water. The residue on the cathode is detached, washed with water, alcohol and dried at 70° and weighed.<sup>1</sup>

**Determination of the Zinc.**—In the liquid from which the nickel has been removed, mixed with the wash water contained in the beaker after the nickel is separated, to about 150 c.c., the zinc is determined by one of the methods indicated for the electrolytic determination of zinc in ordinary brassy alloys (p. 224).

## 2. Determination of the Nickel.

from which the ferric hydroxide has been separated is treated with excess (about 50 c.c. of reagent are required per 0.1 gram nickel) of alcoholic solution of dimethylglyoxime. The solution is heated for 30 minutes on the water-bath and—after the completion of the precipitation has been ascertained by pouring a fresh quantity of the reagent down the sides of the beaker—filtered through a tared Gooch crucible, which is repeatedly washed with hot water, dried at  $120^{\circ}$  and weighed: (weight of the nickeloxime)  $\times 0.2032$  = nickel.

**3. Determination of the Zinc.**—The filtrate from the nickel precipitation is evaporated on a water-bath with nitric and sulphuric acids to eliminate the excess of alcohol and destroy the excess of dimethylglyoxime. The residue is taken up in water, the solution neutralised exactly with ammonia and treated with 8–10 drops of 2N-hydrochloric acid, and the zinc precipitated as in the gravimetric analysis of ordinary brasses.

**4. Determination of the Cobalt.**—The liquid freed from zinc sulphide is evaporated to 50–60 c.c., neutralised with ammonia and treated at  $40^{\circ}$  with a current of hydrogen sulphide. The cobalt is precipitated as sulphide which is converted into sulphate and the latter weighed.

Some types of argentans contain also silver (3–10% or even more). In this case, the silver is precipitated as chloride before the copper is determined (see Determination of Silver in Commercial Copper). The filtrate from the silver chloride is evaporated in presence of nitric acid to expel excess of hydrochloric acid, the residue being dissolved in water and treated subsequently as above.

Further, manganese is sometimes present. In this case, the tin, lead, and copper are determined by the methods given for complex brasses. The iron and manganese are then precipitated with hydrogen peroxide and ammonia, the filtrate being employed for the determination of the nickel and zinc as already described. The iron and manganese precipitated with hydrogen peroxide and ammonia may be separated and determined electrolytically or volumetrically (see Complex Brasses); or the ferric and manganese oxides may be weighed together, then dissolved in hydrochloric acid, and the iron separated as ferric acetate.

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As is seen from the following table (Lunge), alloys of copper, nickel and iron vary in composition according to their origin, purpose, etc.

TABLE XXXV  
Compositions of Argentans

	Cu	Ni + Co	Zn	Mn	Fe

processes. The alloy is analysed like argentan. Usually, however, to determine only the layer of silver and this may be effected as

**Estimation of the Silver.**—1. After being well cleaned and freed from grease the object is suspended by a platinum wire in a 2–3% potassium cyanide solution in a tall, narrow cylinder and is connected with the positive terminal of a current source. A thin, clean copper sheet in communication with the negative pole, is also suspended in the liquid but not in contact with the object. The current (0.1–0.2 ampere) dissolves the silver from the object and deposits it on the copper. When the de-silvering is complete the object and the silvered copper are removed and washed, the silver is then dissolved in nitric acid, the solution diluted and the silver precipitated by a slight excess of hydrochloric acid; the silver chloride is filtered, washed in a Gooch crucible, washed, dried and weighed.

2. The cyanide solution is acidified with dilute hydrochloric acid (pH 1–2), the liquid evaporated until cyanogen compounds are completely removed, and the precipitated silver chloride weighed. From the two quantities of silver chloride the amount of silver on the object is calculated.

3. The object, or part of it, is freed from grease, weighed, and gently heated in a mixture of 9 vols. of conc. sulphuric acid and 1 vol. of conc. nitric acid. By this means all the surface silver is rapidly dissolved, whilst the rest of the object is not at all or but little attacked. When the de-silvering is complete the object is withdrawn, washed rapidly and thoroughly with water and weighed. The loss in weight gives the silver plating. For a more rigorous determination the silver dissolved may be estimated by precipitating with water the nitric-sulphuric solution, together with the object, and determining the silver either volumetrically by the mercuric iodide method or gravimetrically as chloride.

## ALUMINIUM AND ITS ALLOYS

On account of its lightness and stability, aluminium is now used for making many objects in common use and for naval and flying construction. Aluminium forms a constituent of numerous alloys, many of which are mechanically superior to pure aluminium. Among these are: *Light metal* (Al with 3–8% Cu); *Magnalium* (Al with 3–15% Mg); *Alloy* (Al with 10% Sn); *Ziskon* (Al with varying proportions of copper); *aluminium-nickel* (Al with 1–3% Ni); *aluminium-manganese*

After washing is effected by taking the object quickly from the acid mixture



0.5% Mg); *Zirconium* (Al with varying quantities of Cu, Sn, Zn); *Aluminum* (Al with 10-20% Sn, 4-6% Cu). There are also many other alloys of aluminium, nickel and iron; aluminium, copper, lead, nickel and iron.

For commercial aluminium and its more important light alloys, a general method of analysis will be indicated, whilst for light aluminium-bronze and for magnalium, which could also be analysed by the general method, special and quicker methods are given.

For aluminium-copper alloys in which the copper predominates (aluminium-bronzes, aluminium-brasses, etc.), reference should be made to copper and its alloys and for iron-aluminium alloys (ferro-aluminums) to ferro-metallic alloys.

## ALUMINIUM

The elements usually present as impurities in commercial aluminium are copper, lead, iron, zinc, carbon, silicon and sodium. To form the so-called *light alloys*, the aluminium may be associated with tin, copper, nickel, cobalt, manganese, lead, magnesium, etc.

Thus, the analysis of commercial aluminium or of its lighter alloys includes <sup>1</sup>:

**1. Determination of the Copper, Lead, Iron, Zinc, Manganese and Cobalt.**—A. IN ABSENCE OF NICKEL. From 2 to 4 grams of the sample—according as the extraneous metals are present in larger or smaller portions—in minute fragments are treated in a flask (about  $\frac{1}{2}$ -litre) with five times their weight of tartaric acid and a little water. The flask is covered with a small funnel and a small quantity of hydrochloric acid diluted with an equal volume of water added drop by drop. The action is started by gentle heating and sometimes proceeds so vigorously as to require cooling. When the evolution of hydrogen begins to slacken, a fresh quantity of hydrochloric acid of the same concentration is added and the flask is heated on the water-bath until the action is complete, care being taken to use the least possible amount of acid. The heating is then continued for some time, with addition of 2-3 c.c. of conc. nitric acid.

The solution, which is usually turbid owing to the presence of iron and silica, is treated with small quantities of 50% sodium hydroxide solution until the voluminous aluminium hydroxide precipitate at first formed redissolves in the excess of the reagent. Hydrogen sulphide is then passed through until the supernatant liquid becomes faintly yellow and the solution is boiled for some minutes to facilitate separation of the sulphides, leaving a time on the water-bath and filtered into a 300 or 500 c.c. measuring flask, the precipitate being washed with hot water containing a few drops

by heating on a water-bath and the clear liquid treated with a dimethylglyoxime solution in slight excess. After a short water-bath the precipitate is collected in a Gooch crucible, washed with hot water containing a little ammonia and ammonium tartrate with hot water alone until the filtrate is neutral, dried at  $120^{\circ}$ : nickeloxime  $\times 0.2032 =$  nickel.

The residue is heated on a water-bath to expel the alcohol and then with just sufficient hydrogen sulphide to precipitate the metals in the subsequent procedure being as in A (above).

**Determination of the Tin.**—The sodium or ammonium sulphide solution in the 300 or 500 c.c. flask is made up to volume and an aliquot (100 or 150 c.c.) treated, in a  $\frac{1}{2}$ -litre flask covered with a small funnel, with small quantities of hydrochloric acid and with shaking until the residue is dissolved. A further quantity of 25–30 c.c. of conc. hydrochloric acid is added and the liquid boiled, if necessary with addition of a few crystals of potassium chlorate, until the tin sulphide at first separating redissolves in the excess of hydrochloric acid.

The solution is then treated with 25–30 grams of ammonium oxalate and allowed to stand at  $50$ – $60^{\circ}$  to determine the tin (*see* Electrolytic Determination in Ordinary Bronzes).

**Determination of the Carbon.**—This is carried out directly on a weighed sample by either the Corleis method or the copper chloride method (*see* Determination of Total Carbon in Iron).

**Determination of the Silicon.**<sup>2</sup>—1 gram of the aluminium in the sample is dissolved in 300 c.c. of a mixture of 100 c.c. of nitric acid (D 1.2), 300 c.c. of hydrochloric acid (D 1.2) and 600 c.c. of 25% sodium hydroxide. When the action comes to an end, the liquid is heated on a sand-bath until abundant white sulphuric acid fumes appear. The residue is taken up with water acidified with sulphuric acid, dissolved, dissolve the aluminium sulphate and filtered, the vessel and filter washed first with water acidified with sulphuric acid and then with water. The residue on the filter, consisting of silica, graphitic silicon and alumina, is dried, ignited and fused with sodium carbonate, the residue being dissolved in water acidified with hydrochloric acid and evaporated to dryness; this treatment with hydrochloric acid is repeated three times and the residue finally heated in an oven at  $135^{\circ}$  to render it completely insoluble (*see* Iron, 2).

The amount of lead present is determined electrolytically under the conditions indicated for the determination of the nickel.

Reference to I. O. Handy: *Journ. Amer. Chem. Soc.*, XVIII, p. 736.

In the case of lead, the washing is carried out first with hydrochloric acid (D 1.2)

in a platinum crucible and weighed; it is then evaporated on a water-bath with a few drops of sulphuric acid and a few c.c. of hydrofluoric acid, heated to redness and weighed. The loss in weight gives the silica :  $\text{SiO}_2 \times 0.4693 = \text{Si}$ .

**5. Determination of the Sulphur, Arsenic and Phosphorus.**—10 grams of the sample are introduced into a flask fitted with a tapped funnel and a gas-delivery tube connected with absorption bulbs containing bromine water, and very dilute hydrochloric acid slowly run in through the funnel until the metal is completely attacked. The sulphur, phosphorus and arsenic are oxidised by and retained by the bromine water, one-half of which is used for the determination of the sulphuric acid by precipitation with barium chloride. The second half is freed from the excess of bromine and the arsenic precipitated by means of hydrogen sulphide and determined as usual. The filtrate from the arsenic precipitate is freed from excess of hydrogen sulphide and the phosphoric acid then precipitated with ammonium molybdate (*see* Determination of the Phosphorus in Iron).

**6. Determination of the Sodium.**<sup>1</sup>—5 grams of the sample are heated gently with nitric acid (D 1.15), the solution evaporated in a porcelain dish, the residue dried and heated for a long time on a sand-bath, but without melting the sodium nitrate formed. When cold the residue is taken up in boiling water, the solution filtered and the filter washed with boiling water, the filtrate being evaporated to dryness repeatedly with hydrochloric acid to expel the nitric acid and the residue heated to about 300°, allowed to cool, dissolved in water and the chlorine estimated; the corresponding amount of sodium is then calculated.

Lunge<sup>2</sup> observes that a little sodium aluminate is formed under these conditions and advises the treatment of the aqueous solution with ammonium carbonate to precipitate the aluminium and the determination of the sodium as sulphate in the filtrate.

**7. Determination of the Aluminium.**—0.6 gram of the sample, reduced to fine fragments, is treated in a flask covered with a small funnel, with hydrochloric acid diluted with an equal volume of water. When the action is complete, the solution is evaporated in a platinum dish on a water-bath, this evaporation with dilute hydrochloric acid being repeated several times and the residue finally heated in an oven at 135° to render the silica insoluble. The latter is treated with hot water acidified with hydrochloric acid and filtered into a 250 c.c. beaker, in which it is subjected to a current of hydrogen sulphide. The precipitate is filtered off and both vessel and filter washed with hot water containing hydrogen sulphide, the

and ferric hydroxides filtered off, washed, dried and weighed in any manner. This amount, less that of the ferric oxide previously is the alumina and hence the aluminium.

Iron has not been determined previously, it may be estimated of aluminium by means of cupferron.

For purpose, 100 c.c. of the liquid in the flask are treated in a 250 with constant shaking, with 6% aqueous cupferron (ammonium o-sophenylhydroxylamine) until the precipitation of the iron is complete (0.1 gram Fe requires 0.833 gram of the reagent). The end of the precipitation is detected by pouring a little of the reagent down the side of the flask when iron is still present, a reddish-brown precipitate is formed. In the absence of iron a white, crystalline precipitate is formed owing to the low solubility of the reagent in an acid medium.

After precipitation of the iron, the liquid is left for 15-20 minutes to settle, the precipitate being thoroughly washed first with 2N hydrochloric acid, then with slightly ammoniacal water to eliminate all the reagent, and finally with distilled water. The moist filter residue is then carefully ignited in a porcelain crucible, the weight of ferric oxide.<sup>1</sup>

**Determination of the Nitrogen.**—From 3 to 4 grams of the sample are weighed in a flask fitted with a tapped funnel and a gas delivery tube, and treated with sodium hydroxide solution, the gas generated being collected in a gasometer over mercuric chloride. At the end of the action, the flask is boiled for 5 minutes to displace all the ammonia and the nitrogen in the solution. The nitrogen is then determined colorimetrically with Nessler solution, a standard being made with a standard ammonium chloride solution.

\* \* \*

Aluminium of good quality should be white with only a faint blue tint and highly ductile and malleable, while its fracture should be finely crystalline, and free from sponginess or slag. Its specific gravity should be 2.5 and 2.7 (the value increases with the degree of impurity) and the percentage of aluminium at least 97-98, the total amount of elements commonly alloying the aluminium (silicon, iron, copper) not exceeding 1.5-2%. According to Moissan, a particularly harmful influence on the strength and properties of the aluminium, especially when this is to come into contact with sodium, which may be present in the proportion of 0.1-0.2% (Moissan) or, according to some, in even larger amounts (up to 4%). In the Bessemer Foundry, aluminium also contains 0.04-0.12% of nitrogen. The analyses of various samples are given in the following table (Moissan, 1900, Lunge) :

be executed in duplicate.

**1. Determination of the Silver.**—The methods most commonly used are: the dry or cupellation method, Volhard's volumetric method with thiocyanate, and Gay-Lussac's sodium chloride method.

(a) **CUPELLATION METHOD.** This method is based on the fact that the noble metals, silver, gold and platinum, are unoxidisable at the highest temperatures, whilst copper and other metals usually alloyed to the precious metals oxidise easily and, if in presence of a certain quantity of lead—which gives a readily fusible oxide—penetrate by imbibition into the cupel. Thus, the noble metals are separated in the form of a drop, which, on cooling, yields a button capable of direct weighing.

*Apparatus and reagents.* (1) Muffle furnace, either coal or gas, the latter more easy to manipulate and regulate. In order to protect the operator from the intense heat of the furnace, the latter is usually placed in an adjacent room close to the dividing wall, a small aperture in which gives access to the orifice of the muffle.

2. Cupels. These are capsules having the form of an inverted, truncated cone and made with bone dust carefully powdered, calcined, washed and pressed in a mould. A good cupel should absorb its own weight of lead.

3. A thermo-electric couple with the corresponding pyrometer voltmeter, to measure the temperature of the muffle. The couple is placed in the muffle so that its extremity is very close to the cupel.

4. Lead free from silver. That obtained by reducing litharge could be used but its price is too high. Lead almost entirely free from silver is, however, sold and is quite suitable; 20 grams of it should be cupelled as a check.

*Preliminary test.* The amount of lead to be used for the cupellation varies with the silver content of the sample, so that it is necessary to make a preliminary test. The external characters and a test on the touchstone are sufficient to a skilled operator. A beginner may make use of a method which is sometimes employed and which consists in cupelling 0.1 gram of the sample with 0.5 gram of lead if the metal is soft and white, with 1 gram of lead if it is hard, or with 1.5 gram, if it appears reddish.

The amounts of lead to be used for different degrees of fineness are as follows:

Degree of fineness of the alloy.	Amount of lead to cupel 1 gram of the sample
1,000 . . . . .	0.3 gram.
950 . . . . .	3.0 „
900 . . . . .	7.0

the weight of which is allowed for in calculating the amount used, and placed on a tray consisting of a sheet of copper pro-handle and stamped into cavities to take the test pieces. Be-tton is placed the necessary quantity of lead.

s are placed in the muffle and close to them the thermo-electric temperature being then raised to bright redness, that is, to

When these have assumed the temperature of the muffle r the absence of a dark zone between the bottom of the cupel of the muffle), the pieces of lead are introduced into the cupels suitable tongs. The lead at first melts and becomes covered of oxide and after some time *uncovers*, that is, assumes a shiny

lead is uncovered, the test pieces are placed in the cupels with avoid loss by projection, the door of the muffle being left open rmit of observation and to give access to the air. The test nd a shining appearance is resumed. Over the surface of the which is at first only slightly convex, luminous points are seen come absorbed by the cupel. As the cupellation proceeds the creases and the drops of fused litharge, of oily appearance, r and circulate more rapidly. At this point the temperature ssed a little by closing the door of the muffle and increasing the he furnace, in order to oxidise the last particles of lead and ton of silver fused. As the last portions of lead "pass" from e molten metal, which is in a state of considerable agitation, nd of iridescence, this soon disappearing; the button then ue and still, but suddenly flashes out brightly. This indicates ne operation.

s are then gradually brought near to the door of the muffle ttons of silver may cool slowly and rapid release of the occluded d silver absorbs up to 22 volumes of oxygen) not give rise to *bitting or vegetating*) of the metal. After a few minutes the thdrawn from the muffle and the metallic buttons detached, ghtly on both sides, held in tongs and freed with a scratch- he adherent cupel dust and weighed.

weight of the two test pieces in milligrams, if these were each r this weight divided by two, if the samples were 1 gram each, eness of the alloy.

pellation is successful, the silver buttons obtained from the

ples of silver and gold, to obtain the highest accuracy and to be able y, very sensitive balances are employed with an exactly equally divided with very small movable dish-shaped pans, on which the test pieces

white lower ones, and should differ in weight by a few milligrams at the most.

The method of cupellation, largely used for the analysis of argentic minerals and for the control of intermediate products in the extraction of silver as well as for the by-products and for low-grade alloys, is not advisable for analysing ordinary jewellery, coinage, etc., since, however carefully it is carried out, the results obtained are not always concordant and never very exact, mostly somewhat low. The errors are due principally to volatilisation of silver and absorption by the cupel. Tables showing the corrections to be applied have been prepared, but the best method of determining such corrections is to carry out a *check* determination, at the same time and under the same conditions, with pure silver and pure copper in approximately the same proportions as in the sample.

As regards the influence of extraneous metals on the results, it should be borne in mind that gold and platinum *remain with the silver and increase its weight*. They may be detected by treating the button with nitric acid and examining the black powder remaining undissolved. In low proportions, arsenic, tin, antimony, bismuth, iron, nickel and cobalt do not interfere appreciably with the operation.

(b) VOLHARD'S METHOD.<sup>1</sup> This method consists in precipitating silver in nitric acid solution with standard ammonium thiocyanate solution in presence of ferric sulphate as indicator. As soon as the precipitation of the silver is complete, the thiocyanate reacts with the ferric salt and produces a persistent red coloration, which marks the end of the reaction.

*Reagents.* (1) A solution containing 3.1-3.2 grams of ammonium thiocyanate, free from chlorides, per litre.

(2) Cold saturated ferric ammonium alum solution free from chlorides and treated with a little nitric acid to destroy the brown colour; the amount (2-3 c.c.) is used in each titration.

(3) Pure silver (*fine silver*). This may be obtained in foil from reputable firms.

Where many tests are made the fine silver is prepared in the laboratory from the silver chloride residues from Gay-Lussac's method or from silver chloride precipitated from the silver nitrate solutions obtained in the *quantitative* analysis of gold (*see later*). Failing these, commercial silver of 999 fineness dissolved in nitric acid, allowed to stand for some days in the dark, filtered to remove traces of undissolved gold and the silver precipitated with a slight excess of dilute hydrochloric acid.

In whatever way obtained, the silver chloride is washed free from nitric acid, dissolved in ammonia, left for some days and then filtered, the clear solution being made acid with dilute hydrochloric acid to precipitate the silver chloride, which is again washed free from acidity and redissolved in ammonia. After standing for some time, the solution is filtered, treated with sodium hydroxide in the proportion of 750 grams per 1000 grams of the chloride.

with 5 to 10 c.c. of nitric acid (D 1.2) in a conical flask covered until the metal is dissolved and the red fumes have disappeared. removed after cooling and washed with distilled water, the treated with 50 c.c. of cold water and 2-3 c.c. of the ferric and the thiocyanate solution gradually run in from a burette y liquid assumes a persistent pink tint. It is usual to adjust of the thiocyanate solution so that 0.2 gram of silver requires c.

*in the actual test.* Exactly 0.2 gram of the sample is dissolved <sup>2</sup> as described above and the solution diluted and titrated cyanate.

rd method is very rapid and applicable to alloys of any degree is not so exact as Gay-Lussac's method (c). Further, it cannot sence of mercury or palladium, since these metals also react with Also, with more than 70% of copper, the blue coloration renders less exact; in this case fine silver may be added so as to diminish n of copper. Nickel and cobalt have a similar effect to copper.

USSAC'S METHOD. This was proposed in 1832, when the ter of Finance appointed a commission, of which Gay-Lussac er and also reporter, to study the causes of error in the deter-silver by the cupellation method.<sup>3</sup>

s in adding to a nitric acid solution of the sample sufficient de solution to precipitate almost the whole of the silver, and the small amount of silver remaining in solution from the y produced by addition of a fresh quantity of the sodium tion. With a little practice, 1 part in 10,000 may be deter-tely by this method. Since it requires a knowledge of the composition of the sample, a preliminary test by Volhard's y cupellation is necessary.

s. 1. Ordinary bottles of about 200 c.c. capacity, fitted with ground stoppers and with a distinctive mark on both bottle

c.c. pipette. The pipettes used by assayers are usually without to facilitate reading, are fixed in a stand (Fig. 24).

accuracy of measurement is, however, obtained by means of tte (Fig. 25), which is a 100 c.c. pipette drawn out to a point

hod for obtaining fine silver is that adopted by the testing laboratory talian Mint at Rome.

us fumes should be present in the nitric acid used and those formed ction should be completely expelled, since nitrous fumes—and nitric ne hot—decompose thiocyanates.

ac : *Instruction sur l'essai des matières d'argent par la voie humide*, Paris,



glass basin to catch the overflow, while the lower end is connected with a rubber tube and tap with the vessel containing the sodium chloride solution, fixed at a convenient height. The pipette is filled by opening the tap, allowing the liquid to flow gently over. When the liquid begins to overflow at the top, the latter is closed by means of the index finger of the left hand, while the tap is shut and the rubber tube carefully detached with the right hand. The lower end is then touched outside with a dry vessel to remove the small amount of adherent liquid and the bottle placed centrally

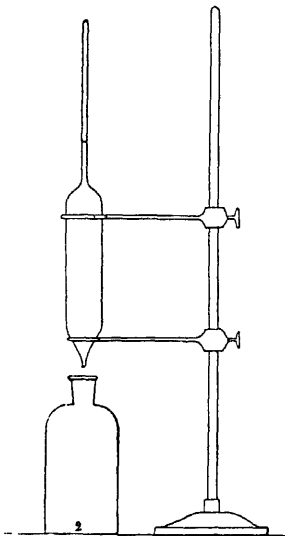


FIG. 24

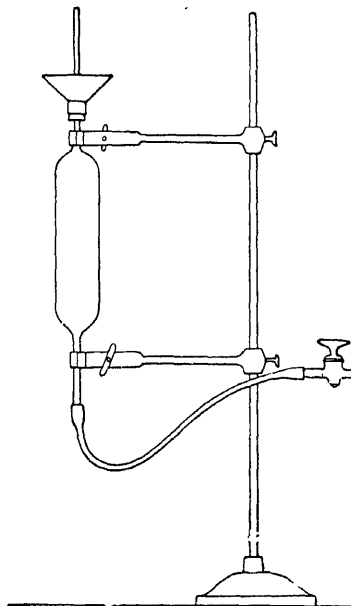


FIG. 25

the pipette. The finger is then withdrawn from the top and all the liquid flows in a continuous jet, but not the drops falling subsequently, and the liquid runs into the bottle.

The pipettes should be kept perfectly free from grease and, before use, should be washed at least twice with the solution to be measured.

3. A shaking apparatus, which may be one of those commonly employed in chemical laboratories for bottles. In assayers' laboratories special forms of apparatus are used to protect the bottles from the action of light. They take 10 bottles at a time and are often, as in the Mint at London, worked electrically. The shaking should be rapid and vigorous.

4. A kind of tray with cells for carrying 10 bottles, scraped from

becomes directly illuminated it is easy to discern the cloud  
the new addition of solution.

. *Standard salt solution*, 100 c.c. of which precipitates almost  
gram of pure silver. It is prepared by dissolving 5.4200  
sodium chloride to 1 litre with distilled water or 5.570 grams  
between filter papers, to 1 litre with ordinary water <sup>1</sup> and,  
case, filtering the solution.

*Standard salt solution*, one-tenth as strong as the preceding  
which it may be prepared by dilution; or 0.5420 gram of  
chloride may be dissolved to 1 litre. This solution, 1 c.c. of  
adds with 0.001 gram Ag, is stored in a bottle fitted with a  
traversed by a pipette graduated from 1 to 5 c.c.

nitric acid, D 1.2, free from chlorine.

*Preparation of the salt solution*. 1 gram of pure silver (fine silver,  
method) is weighed with the greatest accuracy <sup>2</sup> and heated  
in one of the test bottles with 8-10 c.c. of nitric acid (D 1.2)  
is dissolved and the red vapours have disappeared. After  
the neck of the bottle is washed with a few drops of water and 100  
c.c. of standard salt solution introduced by means of one of the pipettes  
being taken that only the liquid falling in a continuous  
stream and not the subsequent drops. The bottle is then stoppered  
and about 10 minutes in the shaking apparatus, the precipitate  
in the liquid becoming quite clear. With a rapid shake the  
precipitate are removed from the upper part of the bottle, the  
bottle is placed on the bench, the stopper removed and 1 c.c. of  
standard salt allowed to flow gently down the side of the bottle.  
The bottle is raised so that the upper portion of the liquid  
is agitated, fresh precipitation of the silver in the form of a cloud  
at the surface of the liquid being usually observed.

The test is exact when this cloud is barely perceptible and when  
by gently shaking the liquid; if there is too much cloud, the  
result must be corrected by addition of salt, whilst, if no cloud  
is observed the solution must be diluted. Only the first case will be con-  
sidered. The second may be reduced by suitable dilution to the first.  
Addition of 1 c.c. of the weaker standard salt produces too intense  
a cloud. The bottle is shaken in the apparatus for 10 minutes and, after  
adding with a further 1 c.c. of the weaker salt. This process is  
repeated until such an addition causes either no further precipitation or  
a barely perceptible cloud. In calculating the correction, the last  
addition is neglected or taken as only 0.5 c.c. in the first case, but must  
be taken into account in the second case. If, for instance, the complete

plus 3 c.c. of the weaker standard salt solution, to every 100 c.c. standard salt it will be necessary to add a quantity of sodium corresponding with that contained in 3 c.c. of the weaker standard (0.000542  $\times$  3) gram if pure salt has been used, or (0.000557  $\times$  3) gram with sea-salt. After this new quantity of salt has been added and dissolved, the resulting solution is tested to ascertain if any small correction is necessary.

The temperature of the standard solution, corrected in this manner, is noted. Each time it is used, it should be well shaken to render it homogeneous.

*Actual test.* We will suppose that the preliminary test of an alloy of silver and copper by Volhard's method gives the approximate fineness 833.4. A weight, 1.201 gram, is taken, this containing very slightly more than 1 gram of silver. Two pieces, each of this weight, are placed in two bottles and treated with 8-10 c.c. of nitric acid (D 1.2) with the precautions mentioned above. When cold, 100 c.c. of the standard salt solution is run into each bottle, which is then shaken, the further procedure being as described for the standardisation of the salt solution. If, in the test, 10 c.c. to the 100 c.c. of the standard salt solution, 1 c.c. of the weaker standard is required, the amount of the silver in the 1.201 gram of the sample will be 1.001 gram, the fineness of the alloy being 833.4 (1201 : 1001 = 833.4).

To obtain greater accuracy, the weaker standard salt solution is added in portions of 0.2 c.c. A practised observer, however, by comparing the intensity of the cloud given by the check with that given by the sample, can estimate accurately by the eye 0.1 c.c. of the weaker standard salt solution. In special works dealing with this subject, tables compiled by Gay-Lussac are given which render unnecessary the calculations. If it happens that the addition of 1 c.c. of the weaker standard salt solution produces no cloud, it is best to repeat the test with a larger quantity of the weaker standard.

Gay-Lussac's method, although expeditious, is undoubtedly the most accurate of all and is universally employed for the control of silver coinage. The accuracy of the results depends on the accuracy of the weighing, particularly on the accuracy with which the standard solution is measured (1 c.c. = 0.5 milligram Ag). It is necessary also to allow for variations of temperature, since at different temperatures the amount of sodium chloride contained in 100 c.c. of the standard solution varies appreciably (1° higher or lower introduces an error of about 0.2 in the fineness). To eliminate this error, Gay-Lussac tried weighing the standard solution instead of measuring it, but found this procedure so much less expeditious that he discarded it, and compiled a table giving corrections for temperature. In practice the means of avoiding such an error is to carry out, at the same time, a

used in the Brussels mint, is rather more delicate than that, but it requires perfect expulsion of the nitrous vapours and means to prevent access of light to the tests, etc.

The Gay-Lussac method is carried out as described above, the silver nitrate being suppressed and identical conditions employed in the test and that on the sample, all causes of error are eliminated. In the influence of extraneous metals, it must be borne in mind that the accuracy of the results, as it also is precipitated as mercurous sulphide. When tin, antimony or bismuth is present, an opalescent solution in which it is difficult to observe the formation of cloudiness. When antimony or bismuth a little tartaric acid (1-2 grams) is added, if the alloy contains tin or a large proportion of lead, it is advisable to add sulphuric acid. Further, gold in proportion exceeding a fineness of 1000 influences the results as it withholds a little silver. Copper in proportion of more than 50% gives coloured solutions, which render observation

**Test of the Gold.**—In a flask with a long, narrow neck, the sample are dissolved in 80-100 c.c. of nitric acid (D 1.2), the liquid being decanted off and the residue again boiled with nitric acid and also decanted. The residue is washed repeatedly with hot water and the undissolved gold remaining as a black powder is transferred to a tared, unglazed crucible (*see* Gold and its Alloys—Quartation) and weighed.

**Test of Tin, Antimony, Copper, Bismuth and Lead.**—The sample are treated with nitric acid (D 1.2). In presence of tin, antimony, or bismuth, the liquid is opalescent or contains a slight white precipitate. The filtered solution is rendered alkaline with ammonia, it becomes more or less intensely blue if copper is present, whilst a flocculent precipitate forms in presence of bismuth or lead, which may be identified by the usual means.

\*  
\* \*

Crude silver often contains small quantities of gold, lead, mercury, arsenic and sometimes selenium and bismuth. The presence of these is extremely harmful, alloys made with silver containing only traces of these are rough and brittle. Refined silver is usually very pure, the average fineness, on the average, 99.9% Ag.

Silver is especially alloyed with copper for jewellery, coinage, etc. The Italian 5-lire pieces is 900 fine with a variation of 2 either way, the French is usually 900 fine, and that for jewellery 800 or even less—

the more important commercial products are gold in bars, granules, powder, etc., and its alloys with copper alone and with silver and copper.

## GOLD

The essential determination to be carried out on the metal is the gold, the fineness being the amount of gold per 1000 parts of the alloy. This determination is made as in alloys of gold and copper (*q.v.*).

## ALLOYS OF GOLD AND COPPER

The most important determination is :

**1. Determination of the Gold.**—By cupellation in presence of lead the gold is separated from copper and other ordinary metals with which it may be alloyed, but not from silver, which resembles gold in being not oxidisable at the highest temperatures. To eliminate the silver, which always accompanies gold in larger or smaller proportion, it is necessary to treat with acid. Experience has shown that, for the complete elimination of the silver, the latter must be in considerable excess, namely, 10 parts to 1 part of gold. It is, therefore, necessary, *before cupellation*, to add silver to make this relation hold. The assay of gold hence consists of two distinct operations :

(1) Cupellation in presence of lead and silver to eliminate the base metals and to form the alloy of gold and silver in the above proportion, an operation termed *inquartation*, since the gold constitutes about one-fourth of the resulting alloy.

(2) Treatment of the latter with acid to remove the silver, this operation being known as *parting*.

To calculate the quantities of silver and lead to be used in the cupellation, the gold content of the sample must be known approximately. It is necessary, therefore, to make a preliminary assay and this is usually done by means of the touchstone.

**PRELIMINARY TOUCHSTONE ASSAY.** This consists in tracing streaks with the sample on the touchstone beside streaks traced with gold or alloys of known fineness and comparing the colours of the streaks before and after treatment with acid.

This test requires :

(1) *The touchstone.* A good stone should be unattackable by acids, should be of a uniform black colour, hard, of fine grain and opaque.

between 350 and 500, the 750 acid for finesses 500-750, and finesses above 750. The compositions of these acids are :

	750 acid.	900 acid.
(1384), 40	Nitric acid (D 1.346), 98	Nitric acid (D 1.384), 40
	c.c.	c.c.
acid (D	Hydrochloric acid (D	Hydrochloric acid (D
	1.171), 2 c.c.	1.19), 5 c.c.
20 c.c.	Distilled water, 25 c.c.	Distilled water, 15 c.c.

re consists in rubbing the sample on the stone so as to leave 4 mm. wide and 15-20 mm. long, and quite close to this, with two needles one less and the other more fine than the characters of the alloy would indicate for it. The streaks are light and compared. A little of the acid corresponding to the comparison needles is then rubbed with a glass plate, which are then compared, dried with absorbent paper, dried with acid, again dried, and the residues of gold on the stone compared. From the colour of the streaks before treatment with acid and of those remaining after the action of the acid, the approximate fineness of the alloy is judged. If the streak left by the sample is lighter than those of the needles, the test must be repeated with a finer or lower fineness.

**ST. Apparatus and reagents.** (1) A muffle furnace, cupels, electric couple like that used in the cupellation of silver (*q.v.*). (2) A sample of 999 fineness absolutely free from gold, and lead which need not be free from silver.

(3) Resistant pear-shaped flasks with stout, very long necks (assay flasks) made of very fine refractory earth or of unglazed porcelain.

**Assay of silver and lead to be used in the cupellation.** The assay of the sample is carried out in duplicate on 0.5 gram of the sample, and the amount of silver added for the inquartation is about three times (more exactly four times) the amount of the gold. Thus, if the touchstone assay indicates an approximate fineness of 900, the amount of silver to be added to each 0.5 gram of alloy is  $0.9 \times 2.5 \times 0.5 = 1.125$  gram. The silver, which is weighed to the nearest centigram, should be in sheet which is not too thin, and the piece used in each case forms two squares of 0.5 cm. side.

The amount of lead required is also related to the fineness of the alloy and is given by the following table :

ness of  
ple.

Amount of lead (grams) required  
per 0.5 gram of sample.

of about 0.5 cm. side. This is placed between the two pieces of silver and the whole wrapped in a piece of white paper or of thin lead foil (all for the weight in calculating the lead to be taken) and placed in the muffle beside the corresponding quantity of lead.

Meanwhile the furnace is started and the cupels, from which the flux has been blown, introduced. In gold assay there is no danger of silver loss owing to volatilisation, so that a rather higher temperature than for silver may be used. According to T. K. Rose,<sup>1</sup> the most suitable mean temperature is about 1070°, each 5° above this causing a loss of 0.01 on the assay. When the temperature indicated is reached, each cupel is charged with the weighed quantity of lead, which rapidly melts, becomes covered with a layer of oxide and, after a few instants, becomes uncovered and shining. With great care, to avoid spurting, the little parcel of silver and silver is placed in the cupel. The phenomena of the cupellation are identical with those observed with silver; after some time the agitation

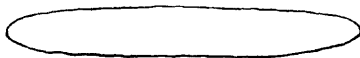


FIG. 26

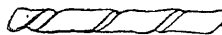


FIG. 27

on the surface is observed, then the iridescence, and finally the bright flame. The cupels are then moved towards the door of the muffle, allowed to cool somewhat and withdrawn, the buttons being detached with a suitable utensil. With successful cupellation, the buttons should be hemispherical, shining and white at the upper part and opaque white at the lower. When a button is held in strong pincers, the edges struck with a hammer and the flat part freed from cupel dust by means of a stiff brush. It is then placed on a clean anvil and struck alternately on the sides and on the flat part, as to give it a somewhat elongated form and is next reheated to redness, leaving it for a short time on a cupel in the front part of the muffle. When cool, it is rolled to obtain a strip (*fillet*) about 0.5 mm. thick and of the shape shown in Fig. 26. This strip, bent in two in a smooth curve, is again reheated to redness for 4-5 minutes on a cupel. When cold, it is twisted into a spiral round a glass rod so as to obtain almost a tube about 0.5 cm. diameter (*cornet*), care being taken that the rolls of the spiral do not touch (Fig. 27). This is then subjected to the operation of parting.

**Parting.** Each of two assay flasks is charged with 25-30 c.c. of nitric acid (D 1.2) absolutely free from chlorine, nitrous fumes and selenium, this being heated to boiling and the two cornets introduced. The heating is continued so as to maintain the liquid in gentle ebullition for ten minutes after evolution of nitrous vapours ceases.<sup>2</sup> After a short rest, the

The residue is again boiled for 10 minutes with 20 c.c. (D 1·3). With the more concentrated acid the boiling is less vigorous bumping may occur, and some authorities recommend a scrap of wood charcoal or a completely charred pepper. If a second portion of acid has been decanted off, a further 10 c.c. of nitric acid (D 1·3) is added and boiled for 10 minutes to destroy last traces of silver. When this last acid together with the insoluble matter have been removed, the cornet is washed with two quantities of 10 c.c. of boiling water, the flask being subsequently filled with cold distilled water. The mouth of the flask is then closed with an inverted crucible of refractory earth or unglazed porcelain, and the flask is firmly on while the flask is inverted. A little water descends and forms a hydraulic seal, while the brittle and slender cornet falls to the bottom of the crucible. After some time, when the fragments detached from the cornet have been deposited, the crucible is raised to the edges of the crucible, displaced a little laterally and movement brought into an erect position. The water is then poured out, the crucible which is dried on the platform of the furnace is then heated to redness in the muffle for 2-3 minutes. Under the heat the cornet contracts to about one-third of its original volume and assumes a golden-yellow metallic appearance. When cold, the cornet is weighed together, the total weight giving directly the weight of the sample; the weights of the separate cornets should not differ by more than 0·5 milligram.

In the assay of gold by cupellation, small losses occur (according to the fineness) owing partly to volatilisation of the gold and partly to absorption by the cupel. This slight loss is, however, compensated by a small amount of silver (0·75-1 one-thousandth) which always remains in the gold in spite of the different treatments with nitric acid. According to Rose, if the operation is properly conducted, the error is not more than  $\pm 0\cdot2$  per thousand. The losses by volatilisation increase with the amount of lead used and, consequently, with diminution of the amount of gold in the alloy; on this account, Riche advises the omission of the treatment with nitric acid in the case of gold-copper alloys of more than 800. In some laboratories the small errors are estimated by making a control assay with pure gold<sup>1</sup> and pure copper in about equal proportions as in the sample, the mixture being cupelled with equal quantities of silver and lead, and the parting carried out under the same conditions. In assaying commercial fine gold Riche advises the addition of 1 per thousand of copper to prevent brittleness in the button



of twice as much lead as is indicated in the table ; after the parting cornets are weighed, again subjected to inquartation with silver and per 1000 of copper and again parted with acid of D 1.3, these operations being repeated until the cornets are of constant weight.

Palladium has no injurious effect, since it dissolves completely in acid.

Iridium causes the formation of black spots on the button, these remaining even after parting. If the gold is dissolved in aqua regia, the iridium remains undissolved and may be collected and weighed.

## ALLOYS OF GOLD, SILVER AND COPPER

In the assay of these alloys, three cases are distinguished :

- (1) Rich alloys, in which the proportion of gold to silver is higher than 1 : 3.
- (2) Medium alloys, with a proportion of about 1 : 3.
- (3) Poor alloys, with a proportion less than 1 : 3. The assay of these alloys includes two operations :
  - (1) Cupellation, which gives the gold and silver together.
  - (2) Parting, which gives the gold alone.

**Preliminary test.** In presence of silver the touchstone assay does not always give reliable results (the presence of silver is easily detected by the formation of a slight, white precipitate on the streak when treated with the acid), so that a preliminary assay by cupellation is advisable. This is made with 0.250 gram of the sample and 4–8 grams of lead, according to the supposed richness in copper, the button of gold and silver being weighed. The weight of the sample, less that of the button, gives approximately the weight of the copper. The button is then rolled, the strip treated with nitric acid and the remaining gold weighed ; the proportion of silver is then found from the difference.

**I. RICH ALLOYS.** (a) *Determination of the gold.* This is carried out on two separate portions of 0.5 gram under the conditions given for the determination of gold in gold-copper alloys. The inquartation silver must be diminished in amount by the approximate silver content indicated by the preliminary assay (see p. 287). The amount of lead required is based on the total fineness and on the ratio between the gold and silver (see *Medium Alloys*).

(b) *Determination of the silver.* 0.5 gram of the alloy is cupelled with the quantity of lead used for the determination of the gold, the resulting button representing gold and silver together ; the latter is thus found from the difference.

silver, being taken.  
 If the preliminary assay gives Au 220 and Ag 680 per 1000, the fineness is 900. For this value the table for the cupellation of lead indicates 5 grams of lead, so that 1.25 is taken, and the table for the cupellation of silver would indicate 3.5 grams of lead, so that 2.6 is taken; the total amount of lead taken is thus 1.25 + 2.6 = 3.85 grams.

The buttons obtained are weighed together and subjected to parting. The weight of the silver is given by the total weight of the two cornets and the silver by the weight of the button minus gold).

**ALLOYS.** Two 0.5 gram samples are cupelled as described in the table for the cupellation of silver and with the amounts of lead there prescribed; the fineness of the silver is, however, kept somewhat higher, especially if the fineness of the gold exceeds 50 per thousand. The sum of the weights of the two buttons is the weight of the silver + gold. To separate the silver, the buttons are heated in a flask. In doing so, it is to be borne in mind that, if the fineness of the gold is not more than 50, the two buttons should be parted in the same flask, and that, if the fineness of the gold exceeds 20 per 1000, the buttons should be rolled and reheated in a flask; further, that, before decanting the acid from the flask, the flask should be given a rotary motion, so that the gold dust collects in the bottom; that the third treatment with acid should be omitted and that care is necessary to avoid loss during the descent of the gold into the crucible.

If the fineness of the gold does not exceed 60-80 per 1000, the silver may be separated with greater exactitude by the Gay-Lussac method (see Silver and Gold).

\* \* \*

The gold obtained contains considerable quantities of impurities, especially silver, bismuth, tin, antimony, arsenic, etc. Thus, gold obtained by the Siemens process varies from 865 to 970 fine, whereas that given by the Siemens process has a fineness of 890-900 and contains, besides silver, only traces of gold; gold precipitated by zinc is 600-700 fine and contains considerable proportions of zinc, lead, iron and copper.

Gold reaches the fineness 993-999, but always contains small quantities of silver.

Gold is used more especially alloyed with copper for jewellery, coinage, etc. The legal fineness of the Italian gold coinage is  $900 \pm 1$  and that of the French 916.66. With jewellery, plate, etc., the fineness may vary from 750 to 900.

Gold-silver-copper alloys are also largely used, more especially for special effects in articles of jewellery (green gold: 750 Au, 250 Ag; red gold: 750 Au, 250 Cu).

## GOLD-PLATING

### (Gilding)

**1. Technical Test.**—The surface of the object is rubbed repeatedly with a small piece of very fine glass paper (No. 000) so as to concentrate any gilding at one point of the glass paper. This point is then treated with a drop of conc. nitric and one or two drops of conc. hydrochloric acid and warmed gently over a very small flame until the metal is dissolved. The solution is then washed into a test-tube with 1-2 c.c. of water, the liquid being filtered if turbid and heated with either an equal volume of fresh sulphur dioxide solution or a few drops of fresh stannous chloride solution. In presence of gold, a violet red, varying coloration is observed owing to the formation of purple of Cassius

**2. Test for Small Objects.**—The sample, or part of it, or a number of small pieces, according to circumstances, are heated on the water-bath with nitric acid diluted with an equal volume of water. When the attack of the common metal is complete, the liquid is filtered through a small filter and the residue washed thoroughly with hot water. The filter is then incinerated in a porcelain dish or crucible and the ash treated with 2 drops of conc. hydrochloric acid and 1 drop of conc. nitric acid and evaporated to dryness on a water-bath until the excess of acid is entirely expelled. When cold, the residue is taken up in about 2 c.c. of distilled water and filtered, the filtrate being heated to boiling with an equal volume of sulphur dioxide solution or of a saturated oxalic acid solution or a few drops of stannous chloride solution. If gold is present, the characteristic violet-red coloration of purple of Cassius is observed.

**3. Test for Large Objects.**—After removal of any organic matter, the surface is scraped with a penknife and the scrapings submitted to the preceding test.

## SILVER-PLATING

**1. Technical Test.**—The article to be tested, freed from grease,<sup>1</sup> is touched with a drop of conc. nitric acid and the latter absorbed by a strip of filter-paper. The spot is then treated with a drop of formaldehyde solution (commercial formalin) and a drop of 20% sodium hydroxide solution. In presence of silver, a blackish spot of reduced silver forms either immediately or after some time.

<sup>1</sup> Sometimes objects are covered with a greenish-black deposit of silver chloride.

a number of small pieces, are treated with 8–10 drops of a vols. of conc. sulphuric acid with 1 vol. of conc. nitric acid—a readily dissolves the superficial silver but attacks the metal either not at all or but little. When the attack is over, the ed into a test-tube, mixed with 2–3 c.c. of water, filtered if divided into two portions. To one of these are added 1–2 e hydrochloric acid, which are allowed to flow gently down e tube and form a layer on the surface of the sulphuric acid silver is present, a more or less distinct milkiess is observed nparison with the other portion—at the surface.

**or Large Articles.**—In general the technical test (*see* above) in this case. If, however, the surface or form of the object ifficult the surface or a few scrapings may be treated with uted with an equal volume of water, care being taken to stop soon as the superficial silver coloration disappears. The ution is then decanted into a dish and evaporated to dryness f dilute hydrochloric acid on a water-bath. The residuc is ot water, acidified with nitric acid and filtered through a small, filter, which is repeatedly washed with hot water. A small bt, dilute ammonia is then passed a number of times through the ammoniacal solution divided into two parts, one of which y acid with nitric acid. In presence of silver a slight precipi- re or less marked milkiess is observed.

## NICKEL-PLATING

**cal Test.**—The surface of the article is treated with a drop ochloric acid, a crystal of methylamine hydrochloride being y and heat applied. In presence of nickel, the place attacked exhibits a blue spot which disappears on cooling.

**thylglyoxime Test** (highly sensitive).—After being freed he surface of the object is moistened with one or two drops diluted with an equal volume of water, the acid being sub- hed into a test-tube, rendered alkaline with ammonia, heated ered if necessary and treated with two or three drops of 1% thylglyoxime solution. In presence of nickel, a red precipitate pink coloration is formed.

is applied to an object of copper or brass, a little of the latter n would give a brown coloration and thus mask the nickel such case, after addition of the glyoxime and gentle heating,

The surface of the object or scrapings from it are treated with hydrochloric acid diluted with an equal volume of water and gently heated. The liquid is filtered and treated with a drop of mercuric chloride solution. A white or grey precipitate of calomel or metallic mercury being formed in the presence of tin.

## **ZINC-PLATING**

The surface is heated gently with dilute sulphuric acid and the object is transferred to a beaker and treated with hydrogen sulphide. The filtrate is freed from the excess of hydrogen sulphide, treated with ammonium chloride, rendered faintly alkaline with ammonia, boiled again, filtered. To the filtrate, acidified with acetic acid, potassium cyanide is added. In presence of zinc, a dirty white flocculent precipitate forms either immediately or after some time.

## **LEAD-PLATING**

Scrapings of the surface are treated in a dish with nitric acid, evaporated to dryness and taken up in a few drops of water. The solution is used for lead by means of potassium chromate or iodide.

## **ALUMINIUM-PLATING**

The surface, or scrapings of it, are heated with 10% sodium hydroxide solution. The liquid is diluted somewhat, filtered, acidified with hydrochloric acid and made alkaline with ammonia. A white gelatinous precipitate is formed in presence of aluminium.

## **COPPER-PLATING**

**(on Iron)**

The object or part of it is treated in the cold with conc. nitric acid which dissolves the copper but scarcely affects the iron. The solution is decanted off, diluted and tested for copper with ammonia.

## **BRASS-PLATING**



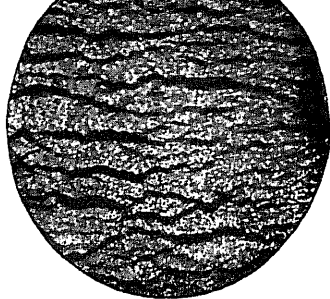


FIG. 28. German sheet



FIG. 29. English sheet

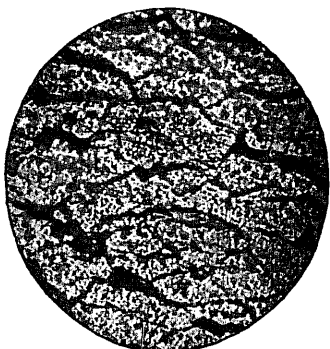
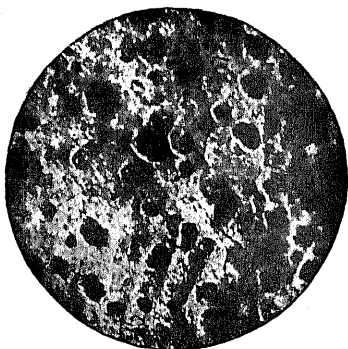
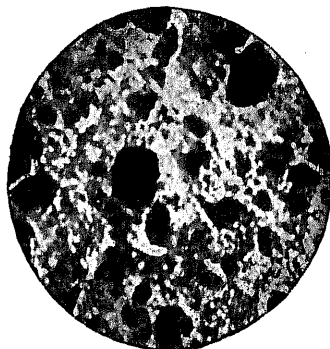


FIG. 30. Belgian sheet



FIG. 31. Belgian sheet (at bend)



is heated and filtered. In the filtrate, acidified with acetic acid, is tested for with potassium ferrocyanide.

## OXIDISING

used for protection against atmospheric agencies or for the sake of appearance, many objects are coated either chemically or mechanically with a layer of oxide, which imparts to them a brown or bluish-brown color.

Artificial oxidation may, however, arise spontaneously during the working of the metal, owing to reheating and it is not always easy to decide if the oxidation is artificial or spontaneous. One distinguishing character is the uniformity of the layer of oxide with artificially oxidised metal in comparison with the irregularity of layers of oxide formed spontaneously. The following tests are based on this criterion.

**Copper and Brass Objects.**—The surface of the object is freed from grease by means of benzene and treated with a drop of mercuric chloride solution. If the layer of oxide is very regular and uniform the reagent will not get into contact with the metal and no reduction is observed. If, however, the oxidation is irregular, the mercuric ion undergoes reduction at the surface of the metal, forming a black deposit.

**Objects of Iron.**—After being cleaned with benzene, the oxidised object is moistened with a drop of 5–6% copper sulphate solution. If the oxidation is irregular and hence not artificially formed, a spot of metallic copper is either immediately or after some time, whereas, if the oxidation is regular and uniform, any reduction which may occur will be observable only after the lapse of a long period.

In connection with this test it is, however, to be noted that sheet metal (Alclad) is now put on the market covered with a regular layer of aluminium oxide of a bluish colour, which, although obtained during the rolling process, is very regular and uniform and does not allow of any reduction by copper sulphate.

The artificial oxidation is nevertheless readily distinguishable from that oxidised metal by the use of reagents or the like.

**Visual test.** When a sheet of this character is bent at right angles the oxide at the bend in the form of scale and shows the naked metal, whereas the artificially oxidised metal exhibits little change.

**Microscopic test.** Further, microscopic examination, in reflected light with a magnification of 100–120 diameters, of the surface of such sheet metal shows a regular, uniform texture, whereas the artificially oxidised metal shows a rough, irregular surface.





## CHAPTER VI

### FUELS

side wood, which is rarely examined as to its value as a com-  
bustible. Fuels used industrially are mainly *coal*, *charcoal* and *mineral*  
fuels. The coals are distinguished according to the degree of  
carbonisation as *peat*, *lignite*, *bituminous coal* and *anthracite*.  
Coke as a fuel is also made of *coke*, the residue of the dry distillation  
of coal, the volatile products being illuminating gas, ammonia  
and *tar*. *Coal-briquettes* (briquettes) are also largely used at the present time ;  
they are formed by the compression in moulds of fragments of different  
kinds of coal with the addition of cementing materials. In this way waste  
coals are utilised and coal which is inconvenient to use on account of  
its condition rendered more useful.

The physical and technical value of coal are determined by *chemical*  
*and calorific examination*. The methods adopted are the same  
as for oils and are described below under the heading : General Methods.  
The experimental data will then be given relating to each of the different

samples, selection of the sample is of great importance.

—Coal is usually far from homogeneous, and care must be  
taken that the sample for analysis represents as closely as possible the mean  
of the whole of the parcel to be examined. When the sample  
is taken from a mine or from a large quantity, portions are taken with  
from different, regularly distributed points of the mass, a large  
quantity thus collected. The larger lumps of this are broken up and  
thoroughly mixed and spread out in the form of a square and the diagonals  
drawn. Two opposite triangles are then discarded and the  
remainder, further disintegrated and mixed, formed into another square.  
These operations are repeated several times until a sample of about 2 kilos  
of this being reduced to small pieces and stored in dry, tightly

When, however, the laboratory is supplied with a limited  
quantity of the latter is broken up and stored as above.

For use, a portion of the sample thus prepared sufficient for the  
analysis to be made (about 200 grams) is reduced to coarse powder  
separately in a dry, air-tight vessel. For each single determina-  
tion this sample is powdered to the degree of fineness requisite in  
the analysis being taken not to throw away any part. Consequently,

## GENERAL METHODS

### 1. Chemical Analysis

This usually includes determinations of the moisture, ash, coke and volatile substances, and sulphur (*see* 1, 2, 3 and 4). Of interest in some cases are determinations of the phosphorus, carbon and hydrogen, nitrogen and oxygen (*see* 5, 6, 7 and 8).

**1. Determination of the Moisture.**—About 5 grams of the substance, not too finely powdered (say, to pass through a sieve of 250 meshes per sq. cm.), are dried in an oven at 105–110° to constant weight, the sample being placed in a covered platinum dish or crucible or between two watch-glasses; as a rule the drying does not require more than two hours. Since dry coal dust, especially that of highly bituminous coal and lignites, tends to oxidise in the air, any increase in weight should be neglected and the preceding weight taken as constant. In such cases, when highly exact determinations are required, the drying should be carried out in a boat in a current of carbon dioxide.

With washed coal, peat and certain earthy lignites, the determination of the hygroscopic moisture is preceded by that of the *water of imbibition*. For this purpose, a large quantity (at least 1 kilo) of the coal, coarsely ground and weighed, is left to dry in the air, the diminution in weight representing the water of imbibition. The substance thus obtained is powdered and used for determining the hygroscopic moisture and other constituents.

**2. Determination of the Ash.**—From 2 to 5 grams of substance (that used for the determination of moisture will serve) are incinerated either in a platinum dish in a muffle or in an open, inclined platinum crucible resting on a perforated asbestos card over a bunsen flame, care being taken to heat gently at first to drive off the volatile substances and to increase the temperature gradually to redness.

In some cases the ash is analysed chemically to determine its principal components and its alkalinity; it may also be examined from the point of view of its fusibility.

**3. Determination of the Coke and Volatile Substances.**—1 gram of the substance (coals rich in volatile matters are best coarsely powdered, say to pass through a sieve of 100 meshes per sq. cm.) is weighed in a platinum crucible 30–35 mm. high, which is placed covered on a triangle of platinum wire arranged so that the bottom of the crucible is 3 cm. above the apex of a bunsen burner giving a flame 18–20 cm. high. When the

that of the sulphides) remains in the ash, whilst the remainder (sulphur and part of that of the sulphides) passes over among the products of combustion (combustible, injurious or volatile sulphur) as sulphur dioxide and, in small proportion, sulphur trioxide.

The determination of sulphur is determined by a slight modification of Eschka's method and is carried out as follows: About 1 gram of the finely powdered sample (passing a sieve of 650 meshes per sq. cm.) is thoroughly mixed in a platinum crucible with about 1.5 gram of a mixture of sodium chloride (2 parts) and dry sodium-potassium carbonate (1 part). A small piece of platinum wire, about 0.5 gram of the same mixture being attached to the top. The open and inclined crucible is then arranged on a stand over a piece of asbestos board and heated over a small flame so that the lower portion is reddened. The heating is continued for about 15 minutes—the mixture being frequently stirred with a platinum wire. When the grey colour has changed uniformly to yellowish, reddish or brown, the crucible is then allowed to cool and the contents washed with water into a beaker and the liquid made feebly yellow with a little nitric acid, boiled, and filtered, the residue being washed with boiling water. The filtrate is acidified with hydrochloric acid, boiled to expel the free bromine, and the colourless liquid precipitated with barium chloride and the barium sulphate weighed as usual.

If both fixed and volatile sulphur are required separately, the former is determined directly. To this end, a weighed quantity of the coal sufficient to give 0.5 grams of ash is incinerated and the ash treated in the hot in a beaker with hydrochloric acid and a little potassium chlorate or potassium dichromate to oxidise any sulphites formed as well as the sulphides. The free chlorine or bromine is expelled by boiling, the liquid precipitated with barium chloride and filtered, and the filtrate acidified and precipitated with barium carbonate in the usual way:  $\text{BaSO}_4 \times 0.1374 = \text{S}$ . Total sulphur = fixed sulphur + volatile sulphur.

**Determination of the Phosphorus.**—This is carried out on the residue from the determination of sulphur, which is digested with conc. hydrochloric acid in a porcelain dish on a water-bath, evaporated to dryness and the residue moistened with water, acid, diluted with water, filtered into another porcelain dish and evaporated to dryness with several additions of nitric acid. The residue is then taken up in water acidified with nitric acid and precipitated with ammonium molybdate and so on (*see* Determination of Phosphorus, p. 173).

**Determination of the Carbon and Hydrogen.**—These are determined by the ordinary method followed for the elementary analysis of organic substances, the substance being burnt in a current of oxygen and

used. About 0.4 gram of substance, not too finely powdered, is used. At the beginning of the combustion, it is well to heat moderately and in a current of air rather than of oxygen; when the volatile products are burnt—this being easily judged from the aspect of the coke remaining in the boat—the fixed carbon is burnt at a high temperature in a current of oxygen. If the undried substance is employed, the moisture content must be allowed for.

**7. Determination of the Nitrogen.**—This is made on 0.75–1 gram of the finely powdered sample by Kjeldahl's method (*see* Fertilisers, p. 123).

**8. Determination of the Oxygen.**—This is calculated by difference, the percentages of carbon, hydrogen, nitrogen, volatile sulphur, ash and moisture being added and the sum subtracted from 100.

## 2. Determination of the Calorific Power

The *calorific power* of a fuel, is the quantity of heat generated by the complete combustion of 1 gram of the fuel, expressed in small calories.

The *small calorie (cal.)* is the amount of heat necessary to raise by 1° C. (more exactly from 0° to 1°) the temperature of 1 gram of water. Some refer the calorific power to 1 kilo and use as unit of heat the *large calorie (cal.)*, which is the amount of heat required to raise by 1° C. the temperature of 1 kilo of water; the numbers are the same in the two cases.

In some cases also the *evaporative power* of a fuel is calculated, this representing the number of kilos of water at 0° which could be transformed into aqueous vapour at 100° by the combustion of 1 kilo of the fuel. Since each kilo of water requires 637 large calories (100 to bring it from 0° to 100° and 537 to transform it into steam also at 100°), the evaporative power is obtained by dividing the calorific power by 637.

The calorific power of a fuel may be calculated approximately from the chemical composition, but it is best to determine it directly by calorimetric methods. The calorific value is referred, according to circumstances, to the fuel as such or simply dried, or to the pure fuel (moisture and ash being deducted).

**1. Calculated Calorific Power.**—Formulæ derived from that of Dulong are used, but the results are only moderately satisfactory. According to Mahler,<sup>1</sup> that to be preferred is the following, which gives, with most coals, errors not exceeding 3%:

$$p = 8140C + 34500H - 3000(O + N),$$

where C, H, O and N are the respective quantities of carbon, hydrogen, oxygen and nitrogen contained in 1 gram of the pure fuel (moisture and ash deducted) and  $p$  is the required calorific value, referred to the pure fuel.

of coals with a high degree of approximation is that proposed namely :

$$p = 82C + aV,$$

calorific power of the fuel as such, C and V are the percentages of carbon (coke less ash) and volatile matter (less moisture) and  $a$  a constant expressing the calorific power (divided by 100) of the volatile matter corresponding with the amount of these volatile matters. To determine the value to be ascribed to  $a$  the percentage  $V^1$  of volatile matters supposed free from moisture and ash is calculated by the formula,

the corresponding value of  $a$  is then obtained from the

table :

$a$	$V^1$	$a$	$V^1$	$a$	$V^1$	$a$
100	14	120	23	105	32	97
145	15	117	24	104	33	96
142	16	115	25	103	34	95
139	17	113	26	102	35	94
136	18	112	27	101	36	91
133	19	110	28	100	37	88
130	20	109	29	99	38	85
127	21	108	30	98	39	82
124	22	107	31	97	40	80
122						

**Calorimetric Determination of the Calorific Power.**—The direct methods are undoubtedly to be preferred to those indirect as they give far more certain results.

Various forms of apparatus devised for such determinations may be divided into three classes : (1) calorimeters in which the combustion takes place in a stream of air or oxygen at the ordinary pressure, like those of Berthelmann, Alexejew, Schwackhöfer, and F. Fischer ; (2) calorimeters in which the combustion occurs with the aid of an oxidising agent mixed with the fuel, as in those of Lewis Thompson, Stohmann, and (3) calorimeters in which the combustion is effected with oxygen at high pressure and volume and very high pressures, known as *calorimetric bombs* ; the first bomb was due to Berthelot and Vieille and on this were based the more practical and cheaper ones of Mahler, Hempel and Kroecker, which admit of various suitable forms of apparatus for exact determinations.

a mark at two litres, and a brass foot fitted with a small cylindrical copper capsule or furnace in which the combustion occurs. The capsule is covered with a copper cylinder with a row of holes round the bottom and a tube with a tap at the top; this cylinder is held in place by four springs on the brass foot. A thermometer reading to  $0.1^{\circ}$ , and protected by a metal guard, is also required.

2 grams of the fuel, ground in an iron mortar to pass through a No. 6 sieve (650 meshes per sq. cm.), are thoroughly mixed on a piece of shining paper by means of a flexible steel spatula with the oxidising mixture (3 parts of powdered, dry potassium chlorate and 1 part of potassium nitrate, carefully mixed without using the iron mortar and passed through a No. 6 sieve), sufficient of the latter being used to give a homogeneous, lead-grey mixture, which should burn completely, regularly and moderately rapidly. The amount of oxidising mixture necessary is usually 20–30 grams per 2 grams of fuel, but it varies with the character of the fuel and should be determined by preliminary trial.

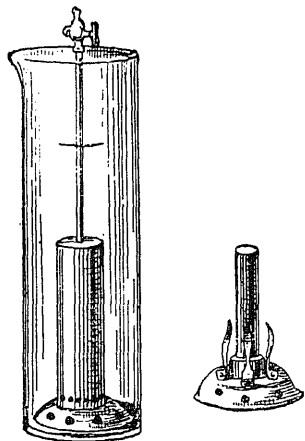


FIG. 34

By means of the spatula used before, the mixture is placed in the copper capsule in such a way as to compress it uniformly and as little as possible; if the quantity of the mixture is too great to be held by the capsule without compression, it is advisable to use only 1 gram of the fuel and the corresponding amount of the oxidising mixture. On the top of the mixture is placed a piece of slow match,<sup>1</sup> which should protrude about a centimetre, the copper cylinder fitted, the tap closed and the whole immersed in the water in the glass cylinder; the water should be, according to circumstances, between  $2^{\circ}$  and  $7^{\circ}$  lower than the temperature

of the air.<sup>2</sup> The water is mixed by means of the apparatus itself and the temperature shown on the thermometer noted; the apparatus is then withdrawn, the match lighted, the cover rapidly replaced and the whole at once placed in the water before the mixture ignites. After a few seconds, when ignition occurs, the gaseous products issue turbulently from the holes in the cover and escape upward through the water.

burn with difficulty, while peat and many bituminous lignites completely.

Thompson calorimeters of English construction, the amount of the glass cylinder weighs 29,010 grains (1879.85 grams). When 4 grams) of the fuel are burnt, since  $29010 \div 30 = 967 = 537$  rise in temperature in Fahrenheit degrees (increased by one- directly the grains of water at  $100^{\circ}$  transformable into steam heat generated by one grain of the fuel, i.e., the evaporative ed for water at  $100^{\circ}$  and not, as usual, at  $0^{\circ}$ .

pointed out that, in England, calorific powers are mostly expressed the *British Thermal Unit* (B.T.U.), which is the quantity of heat ise the temperature of 1 lb. of water (0.4536 kilo) by  $1^{\circ}$  Fahrenheit. ie = 3.9683 B.T.U. and 1 B.T.U. = 0.252 large calorie. Further, er of  $x$  calories per kilo corresponds with 1.8  $x$  B.T.U. per pound, r pound is equivalent to 0.5555  $x$  calories per kilo.

Thompson calorimeters, the glass cylinder is marked at 2000 2148 c.c. ( $= 537 \times 4$ ). If the latter quantity of water is taken the fuel are used, the rise of temperature (increased by one-tenth), e, will give directly the evaporative power (referred to water at efore not to the standard usually adopted : *see* later).

R BOMB CALORIMETER. This apparatus (Fig. 35), which is t of those employed, consists of a vessel or bomb *a* of fairly mild steel, nickelled outside and enamelled inside : capacity , thickness of walls 8 mm., weight about 4 kilos. The bomb , screwed iron lid *b* with lead packing and furnished in the ferro-nickel conical screw valve *v*. The cover supports the sisting of two platinum rods *e*, one passing through the cover from it and the other fixed directly to the cover and supporting n dish *c* in which the fuel is placed. The two terminals are a small spiral of very thin iron wire which burns on passage (about 2 amps. at 8–10 volts) and so ignites the fuel in contact

rests on supports on the bottom of the brass calorimetric ch contains 2,200 grams of water, a thermometer *t* divided f a degree and allowing  $0.01^{\circ}$  to be estimated, and a spiral protect it from external influences, the calorimeter is placed e-walled metallic vessel *B* filled with water and covered with

a determination, exactly 1 gram of the fuel, not too finely weighed into the capsule *c* and this placed in the bomb after n wire spirals has been fitted to the terminals so that it comes with the fuel. The lid *b* is screwed tightly down, the valve



minutes, ignition is caused by the momentary passage of the current. The temperature is read half a minute after ignition, after a further half-minute, and then each minute until the maximum temperature is reached (after 3 or 4 minutes) and for five minutes during the subsequent fall in temperature.

At the end of the experiment, the tap *r* of the bomb is opened to allow the gas to escape, the bomb itself being then opened and washed out inside

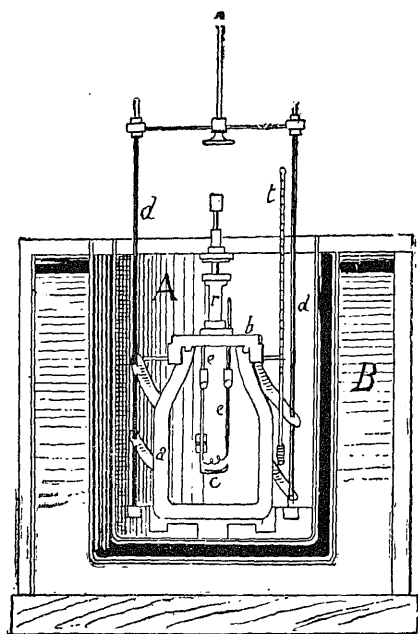


FIG. 35

with a little distilled water.<sup>2</sup> The nitric acid formed from the nitrogen contained in the bomb is determined in the wash water by titration with caustic potash solution (1 c.c. = 0.01 gram  $\text{HNO}_3$ ) in presence of methyl orange. Any sulphuric acid formed is also calculated as nitric acid, but with fuels poor in sulphur no appreciable error is introduced in this way. When, however, allowance is to be made for the sulphuric acid, the procedure is as follows: The wash water is heated for a short time to expel carbon dioxide and titrated with N/10-baryta in presence of phenolphthalein; excess of standard sodium carbonate solution is then added and the excess titrated with N/10-

hydrochloric acid in presence of methyl orange. The volume of baryta solution used corresponds with the sulphuric and nitric acids together, and that of the sodium carbonate solution with the nitric acid alone.

In calculating the results of the measurement, it is first necessary to establish the correction necessary owing to the exchange of heat with the surrounding air in the interval of time between ignition and the attainment

<sup>1</sup> Compressed oxygen, if obtained electrolytically, often contains hydrogen, which appreciably alters the results of the calorimetric experiments. In such case it is necessary to purify it, before admitting it to the bomb, by passing it slowly through a red-hot copper tube and then through a coil cooled with water. On the other hand, oxygen from liquid air, containing appreciable quantities of nitrogen, has the disadvantage of giving rise to the formation of nitric acid, allowance for which must be made in calculating the results.

on ignition and the attainment of the maximum temperature varies uniformly, so that the correction may be referred to the mean temperature of the minute considered. If the mean temperature of the minute differs by less than  $1^{\circ}$  from the maximum, it is neglected; if the diminution of temperature due to loss of heat during that minute is equal to the mean diminution in every minute after the maximal temperature is reached, if, however, the mean temperature of any minute differs from the maximum by more than  $1^{\circ}$  and less than  $2^{\circ}$ , the correction for that minute is taken as the mean diminution after the maximum temperature is reached, and is multiplied by  $0.005^{\circ}$ . Finally, for the first half-minute after ignition the correction is taken as that the variation is equal to the mean observed before the maximum temperature is reached.

In this correction, account must also be taken of (1) the heat of formation of the iron coil,  $1.6$  cal. being allowed per milligram of iron, and (2) the heat of formation of the nitric acid, which is  $0.23$  cal. per milligram (also of the heat of formation of sulphuric acid; in the open calorimeter, nitric oxide will be formed and the correction to be subtracted is  $0.005$  cal. per milligram of sulphur or  $0.73$  cal. per milligram of sulphuric acid).

The calorific power  $p$  (in the case where the sulphuric acid has been replaced by nitric acid) is, therefore, expressed by the following formula:

$$p = (T^1 - T + t)(A + a) - 0.23n - 1.6f \dots (i),$$

where  $T^1$  = temperature before ignition,

$T$  = maximum temperature,

$t$  = correction for heat given up to surrounding air,

$A$  = weight of water in the calorimeter,

$a$  = *water-equivalent* of the apparatus, this being determined once and for all in a preliminary experiment,<sup>1</sup>

$n$  = grams of nitric acid formed,

$f$  = grams of iron in the igniting coil.

In this calculation, it may be pointed out that the various corrections indicated above compensate one another partly, so that, for the purpose of the calculation, the *water-equivalent* of the apparatus may be taken as the weight of water requiring the same amount of heat to raise its temperature  $1^{\circ}$  as the calorimetric apparatus (vessel, stirrer, thermometer, etc.) determined by an experiment with a substance of known heat of combustion (e.g. naphthalene, 9692; cane sugar, 3957; benzoic acid, 6330 cal.).

Between the true calorific power of the substance and that calculated from the experimental results without taking account of the heat absorbed by the calorimeter, the difference is the heat absorbed by the calorimeter, which is deduced by the rise of temperature, gives the required water-equivalent, and is the amount of heat absorbed by the calorimeter. It is highly desirable to allow for the corrections for the rigorously exact calculation of the calorific power of the substance.

corrections are omitted. Under such circumstances the thermocouple readings during the preliminary period and those after the maximum temperature has been passed, and also the titration, becomes useless, the values required being those of the magnitudes in the expression,

$$p = (T^1 - T)(A + a) \dots \dots \dots \text{(ii),}$$

which then gives the calorific power.

It must also be mentioned that, whilst in the bomb the water (hydrogen water plus that formed by combustion of the hydrogen in the fuel) remains in the liquid state, in practice it passes off as vapour among the products of combustion; consequently, the calorific power calculated as above includes also the heat of condensation of the water, which in practice is not utilized. In France the calorific power resulting from the above calculation, taking into account the heat of condensation, is called *gross calorific power*, whereas in Germany, Austria, and elsewhere, the heat of condensation of the water is deducted, the assumption being made that the water remains as vapour (*net calorific power*). Taking 600 cal. as the heat of condensation of 1 gram of aqueous vapour, if H and M are the percentages of hydrogen and moisture in the fuel, the deduction to be made from the gross calorific power to obtain the net value is 6 (M + 9H). Where an elementary analysis is not made, a separate determination may be made of the total water evolved during the combustion (by burning a given weight of fuel in a tube and collecting the water in an absorption apparatus), or, as Mahler suggests, in practice the mean values of H may be taken according to the quality of the fuel tested.

EXAMPLE: The experimental data obtained were as follows:

$$\begin{aligned} A &= 2200 \text{ grams.} \\ a &= 474 \quad \text{,,} \\ n &= 0.125 \quad \text{,,} \\ f &= 0.032 \quad \text{,,} \end{aligned}$$

Temperature observed:

0 minutes	. 15.180°	7 minutes	. 18.250°
1 "	. 15.185	8 "	. 18.305
2 "	. 15.190	9 "	. 18.290
3 "	. 15.195	10 "	. 18.275
4 "	. 15.200	11 "	. 18.260
5 "	. 15.205 (ignition)	12 "	. 18.245
5½ "	. 15.795	13 "	. 18.230
6 "	. 17.850		

Hence  $T^1 - T = 18.305 - 15.205 = 3.100^\circ$ . The law of variation of temperature after ignition is given by

$$\frac{15.205 - 15.180}{5} = 0.005^\circ,$$

and that after the maximum is passed by

$$18.305 - 18.230 = 0.075^\circ$$

$(0.0325)(2200 + 474) - 0.23 \times 125 - 1.6 \times 3.2 = 8296.4$  cals  
without corrections according to formula (ii),

$$p = 3.1 \times (2200 + 474) = 8289.4 \text{ cal.}$$

the gross calorific power is found. If the fuel contains 3% of hydrogen,  $6(3 + 9 \times 4.5) = 261$  cal., must be subtracted to obtain the net calorific power, which is therefore  $8035.4 - 261 = 7774.4$  (uncorrected).

**MAHLER'S CALORIMETRIC BOMB.** This apparatus, which is simpler than that of Mahler, consists (Fig. 36) of a cylindrical, thick-walled iron autoclave *A*, holding 1 litre of water and coated inside with enamel. It has a screw cap *B* which fits air-tight by means of a lead washer and has an outlet valve *a* which is closed by a conical screw plug. The lid carries two rods, *g* and *h*, which are connected directly with it, and are insulated by means of a sleeve *f* from the lid, through the cap. Each rod terminates in a platinum wire bent to a hook *c* and *b* respectively, which support a capsule *d* of refractory material in which is placed the fuel. The capsule is pressed into cylindrical form in a die *p* between the two wires. A very thin platinum wire, *e*, passes through the cylinder of the bomb and terminates in the latter when heated by an electric current.

The calorimeter is a cylindrical vessel *G* containing, besides the water, 1 litre of water and a wooden vessel *H* so that the space between the walls is 2 cm. The bomb is then closed by a cover, *C*, which passes the two terminals, *g* and *h*, to a thermometer *t* to read to  $0.01^\circ$  and a stirrer *m*.

The weighed fuel is pressed into a cylinder weighing about 1 gram. The igniting wire is already pressed. It is weighed exactly and placed in the capsule *d* and the bomb closed, oxygen being then passed in slowly until the pressure becomes about 15 atmos. The valve *a* is then closed

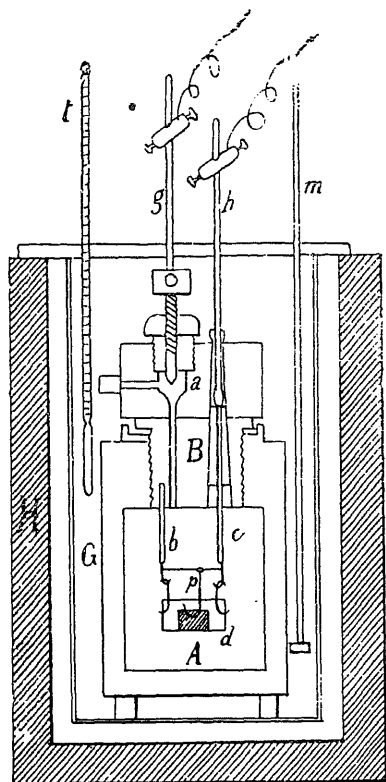


FIG. 36

its maximum. The weight of water, plus the water equivalent calorimeter (usually determined once for all by a preliminary measurement), multiplied by the rise of temperature, gives the heat generated. For a more exact calculation, the corrections indicated for the Mahler apparatus may be introduced.

Kroeker has modified the Hempel bomb by the addition to the bomb of a second valve inserted in a platinum tube leading almost to the bottom of the bomb for the admittance, after the combustion, of a current of dry air into the bomb heated at  $105^{\circ}$  and the absorption of the expelled vapour in a weighed calcium chloride solution. The amount of water thus determined is used in calculating the net calorific power.

## SPECIAL PART

### WOOD CHARCOAL

This is distinguished as *hard* or *soft*, according as it is made from hard or soft wood, and as *red* or *black* according to the degree of carbonization to which it has been subjected. The black, composed principally of cellulose, is in the more common use.

\*  
\* \* \*

Charcoal contains usually 80–90% C, 1–3% H, 2–4% O, 6–10% H<sub>2</sub>O, 1–3% ash. As a rule, its calorific power lies between 6500 and 7500 cal.

### PEAT

This is a fuel of somewhat diverse origins and may, therefore, present a very varied aspect and composition. According to its origin, it is distinguished as *marsh*, *heath*, *meadow*, *forest*, and *marine* peat, and according to its appearance as mucous, spongy, herbaceous, earthy, compact, lumpy, etc.

\*  
\* \* \*

When freshly extracted, peat always contains a considerable quantity of water, which may vary from 50 to 90%, whilst, when air-dried, it still contains 10–30% of moisture. The percentage of ash varies widely and may be as low as 20–30% or even much more.

The best peats have compositions lying between the following limits, which refer to the dry product:

## LIGNITE

in several varieties. Sometimes it has the aspect and colour (wood) and sometimes it is brown, friable and easy to break (*gnite*) ; in some cases it consists of superposed layers (*schistose* others is compact and varying in colour from brown to shining *al*).

\* \* \*

won, lignites contain 20-60% of moisture, and when air-dried, percentage of ash is very variable and, although it usually varies, it may also be much greater. The elementary composition fuel free from ash and moisture, generally varies between the

.	.	.	.	.	.	.	.	55-75%
en .	.	.	.	.	.	.	.	4-7%
.	.	.	.	.	.	.	.	20-35%
n .	.	.	.	.	.	.	.	0.5-2%

es sulphur may be present in marked proportions. The calorific ignites varies from 4,000 to 6,500 cal.

II (see p. 310) gives the analytical results for various lignites.

## COAL

includes the *bituminous coals* and *anthracite* ; there is a on from the one to the other and no sharp delimitation.

the most important industrial fuels. They are usually black, the following types being distinguished : shining, lque, black ; cannel, of a velvety, blackish colour, with a ure ; fibrous coal ; and bituminous slates (boghead).

\* \* \*

their chemical composition, coals are classified, after egories, which differ in the quantity and quality of the coke in their calorific powers. The normal limits for each of these ed in Table XXXVIII (p. 311), the data in which are referred (free from moisture and ash).

TABLE XXXVII  
Composition of Lignites

Quality.	Chemical Composition.							Fixed Carbon.	Volatile Matters.	Calor. Power.
	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Sulphur.	Ash.	Moisture.			
<i>Italian</i>										
Al Gandino, Bergamo)	36.74-51.46	3.72-5.20	15.50-26.86	0.29-1.38	0.84-1.33	2.10-23.71	12.76-25.95	21.17-30.28	37.05-54.86	4060-5168
Volterra) <sup>1</sup>	57.16-63.40	5.01-5.66	25.40-26.68	—	—	5.54-11.15	—	—	—	—
(do.)	—	—	—	—	3.86	6.16	14.55	47.46	31.83	4660
Genoa) <sup>1</sup>	57.38-59.34	4.92-5.55	28-31.98	—	—	3.13-9.70	—	—	—	—
(do.)	—	—	—	—	1.71	7.82	29.78	32.75	29.63	4410
Aboli (Grosseto) <sup>1</sup>	73.44	6.15	15.31	—	—	5.10	—	60.00	34.00	7400
(do.) <sup>1</sup>	—	—	—	—	2.34	6.00	—	—	—	6000
(do.) <sup>1</sup>	60.10	5.23	26.62	—	—	8.05	—	—	—	5550
(do.) <sup>1</sup>	—	—	—	—	0.87-3.03	0.55-7.32	—	53.68-61.85	37.60-39.00	6300
e Morgnano (Spol.)	—	—	—	—	7.28	2.23-22.81	36.09-42.59	17.85-23.75	19.72-38.50	1687
s (Gonnese, Sardinia).	57.95	4.61	8.93	4.26	—	10.87	6.63	39.18	43.32	5477
(do.) <sup>1</sup>	59.98-70.55	4.75-5.25	19.40-29.42	—	—	4.80-5.85	—	46.15-55.15	42.05-48.00	—
<i>From other countries</i>										
Germany) (18 samples)	50.41-55.87	3.76-5.23	18.00-26.31	—	0.27-1.78	2.28-15.96	7.28-16.22	—	—	4550
Thuringia, Anhalt (Germany)	—	—	—	—	—	—	—	—	—	—
ples)	40.00-58.04	3.45-5.98	11.13-24.71	—	0.87-6.03	6.94-25.08	8.47-23.15	—	—	3700
Germany (10 samples)	43.14-57.73	3.43-5.07	12.33-25.56	—	0.44-6.27	4.29-19.62	9.15-14.36	—	—	3870
(10 samples)	50.32-63.97	3.98-5.26	5.60-19.06	—	0.23-10.98	2.12-14.28	1.13-19.86	—	—	4780
ylria)	63.46	4.78	24.30	—	1.47	4.75	0.71	46.95	47.59	6200
jan (Hungary) (3 samples)	44.59-48.02	3.59-3.82	11.30-12.57	0.97-1.06	0.99-1.22	23.42-26.11	11.92-12.00	—	—	4165
y (Hungary)	60.47	4.08	13.57	1.07	2.55	15.63	5.18	—	—	5600
samples)	48.04-54.40	3.53-4.47	10.56-14.90	—	1.62-4.88	15.71-19.25	7.95-12.37	45.10	45.01	4453
(France)	59.80	4.51	25.80	6.75	1.50	12.42	3.14	—	—	5500
the Rhone (France)	62.88	4.58	11.16	—	—	—	—	—	—	5000

## Limits of Composition of Coals (Gruner)

(The values refer to dry, ashless coal)

	Elementary percentage Composition.			Ratio O+N H	Percentage of		Appearance and quality of the Coke.
	C	H	O+N		Coke (fixed carbon)	Volatile Matters.	
ame cak-	75-80	5.5-4.5	19.5- 15.5	4-3	50-60	50-40	Pulverulent or only slightly coherent.
ame	80-85	5.8-5	14.2-10	3-2	60-68	40-32	Caked but very porous.
or	84-89	5.5-5	11-5.5	2-1	68-74	32-26	Caked, somewhat porous.
ame bal	88-91	5.5-4.5	6.5-4.5	about 1	74-82	26-18	Caked and com- pact.
ame coal	90-93	4.5-4	5.5-3	about 1	82-90	18-10	Adherent or pul- verulent.
. coal	93-95	4-2	3	about 1	more than 90	less than 10	Pulverulent.

power of coals, referred to the dry, ashless fuel, varies in general  
900 cal.

the uses to which different coals are especially suited, long flame,  
(Class 1) is adapted to the manufacture of gas and particularly  
furnaces. Gas coal (Class 2) is preferred for making gas, since,  
with the preceding, it gives volatile matters richer in carbon  
illuminating, although in lower yield. Fat, caking or furnace  
for use in reverberatory furnaces and for making metallurgical  
for purpose the short-flame caking coals are particularly adapted.  
a, short-flame or anthracitic coals and the anthracites, owing  
combustion and to the little smoke they give, are used for domestic  
for the heating of boilers, where a slow, quiet fire is required.  
sequence of the paucity of their volatile matters, the anthracites  
directly in blast furnaces instead of coke.

For purposes coal should not contain more than 2-3% of sulphur.  
contain 3-8% of ash and the proportion may be 12% in good  
with more than this is regarded as medium or bad. The moisture  
should not exceed 3%.

X. gives the analytical results for a number of bituminous coals



TABLE XXXIX  
Compositions of Different Coals

	Chemical Composition.							Coke.	Volatile Matter.	Calorific Power.
	Carbon.	Hydrogen.	Oxy- gen.	Nitro- gen.	Sulphur.	Ash.	Moisture.			
<i>British</i>										
Abercrombie : caking coal . . .	84.77	4.98	7.01	4.66	0.55	4.14	0.90	—	—	—
Western Valley : " . . .	83.64	4.59	7.01	1.06	0.71	2.23	0.76	—	—	8058
Ilkley : " . . .	82.32	4.75	4.59	1.03	1.03	6.59	0.72	—	—	—
Seaton : " . . .	83.25	4.96	3.40	1.65	0.79	5.95	—	68.9	—	7956
Seaton's Navigation : Anthracite <sup>1</sup>	90.27	4.12	2.53	0.63	1.20	1.25	—	84.5	—	8131
Seaton : " . . .	89.10	4.75	2.06	1.20	0.85	1.40	0.64	86.5	—	—
Seaton : " . . .	90.06	5.16	2.79	0.79	0.58	0.62	—	86.5	—	8080
Seaton : " . . .	88.30	4.56	2.78	1.50	0.98	1.20	0.68	84.6	—	—
Seaton : " . . .	90.41	4.82	1.71	0.96	0.71	1.39	—	89.1	—	7755
Seaton : " . . .	86.48	4.04	3.62	0.88	0.70	3.04	1.24	81.5	—	—
Seaton : " . . .	89.49	4.00	3.78	0.84	0.84	1.89	—	—	—	7964
Seaton : " . . .	86.36	4.78	2.21	1.37	0.71	3.69	0.88	—	—	—
Seaton : " . . .	84.20	3.90	2.49	1.17	0.96	6.65	0.63	85.2	—	7956
Seaton : " . . .	86.40	4.05	1.97	1.10	0.96	4.57	0.95	84.7	—	8080
Seaton : " . . .	88.83	4.63	2.02	1.10	0.50	2.60	0.32	85.7	—	—
Seaton : " . . .	87.21	4.11	1.75	1.60	1.05	3.68	0.60	—	—	—
Seaton : " . . .	90.61	3.77	2.32	0.98	0.98	2.28	—	91.52	6.20	8589
Seaton : " . . .	91.25	3.60	2.32	0.83	0.83	2.00	—	92.04	5.96	8541
Seaton : " . . .	91.60	3.61	3.25	0.44	1.10	1.10	—	93.60	5.30	—
Seaton : " . . .	94.18	2.99	0.50	0.76	0.59	0.98	—	—	28.4	—
Seaton : " . . .	82.58	4.42	6.64	0.85	0.81	3.47	1.23	71.6	30.4	—
Seaton : " . . .	84.93	5.13	4.92	1.53	1.14	1.48	0.87	69.6	32.2	—
Seaton : " . . .	84.06	5.11	6.34	0.75	0.82	1.36	1.56	67.8	33.3	—
Seaton : " . . .	82.36	5.11	6.56	1.05	0.86	2.04	2.02	66.7	—	—

Ayrshire : Main, Steam coal <sup>1</sup>	79.82	5.82	11.31	0.94	0.86	1.25	49.3	50.7
Lesmahagow : Cannel coal <sup>1</sup>	73.44	7.62	11.77		1.14	6.03	43.3	—
Edinburgh : Boghead <sup>1</sup>	63.10	8.91	7.25		0.96	19.78	—	—
<i>German and Austrian</i>								
Silesia (128 samples)	55.46-81.50	3.82-5.38	5.19-15.23		0.29-2.80	1.77-23.68	0.70-7.99	—
Silesia (24 samples)	61.89-79.26	0.56-4.86	1.74-12.33		0.74-1.67	6.13-33.85	0.81-4.93	—
Provinces and Westphalia (38 samples)	58.82-84.24	3.83-5.48	2.13-11.25		0.71-4.77	3.04-23.52	0.42-7.04	—
Basin (5 samples)	63.00-76.97	4.00-4.97	6.57-10.12		0.79-1.12	9.36-24.12	1.01-4.56	—
Wesphalia (7 samples)	53.04-76.62	3.13-4.91	7.75-10.80		1.03-2.24	5.25-31.04	2.65-6.23	—
Wesphalia (6 samples)	64.09-70.63	3.65-4.83	8.42-17.24		0.92-1.03	2.58-10.98	5.90-10.65	—
<i>French</i>								
(Nord) : Caking coal <sup>2</sup>	83.75	4.39	5.76		—	5.00	1.10	20.20
(Pas de Calais) : Caking coal <sup>2</sup>	87.74	4.68	5.03		0.86	1.55	1.00	19.00
do. Gas coal <sup>2</sup>	83.73	5.22	7.00		—	3.00	1.05	29.55
do. Gas coal <sup>2</sup>	81.27	5.31	8.59		—	3.60	1.23	30.47
Combe (Gard) : Coke coal <sup>2</sup>	87.16	4.27	4.16		—	3.80	0.61	12.79
(Côte d'Or) : Non-caking, long-flame								
do. Gas coal <sup>2</sup>	74.73	5.17	11.75		1.28	4.85	3.50	36.10
do. Anthracitic coal <sup>2</sup>	89.39	3.66	3.70		—	1.45	1.80	10.10
do. Anthracitic coal <sup>2</sup>	80.18	5.25	8.17		0.59	3.40	3.00	37.40
do. Anthracite <sup>1</sup>	94.00	1.49	0.85		—	3.66	—	—
<i>Belgian.</i>								
Buisson (Mons) : Caking coal <sup>1</sup>	83.40	5.40	7.76		—	3.44	—	—
Vue (Mons) : Short-flame, caking coal <sup>1</sup>	86.38	4.48	6.09		—	3.05	—	—
Martin (Charleroi) : " <sup>1</sup>	86.23	4.62	5.81		—	3.34	—	—
Met (Charleroi) : Anthracitic coal <sup>1</sup>	90.89	3.65	3.98		—	1.48	—	—

<sup>1</sup> In these analyses the numbers refer to the dry fuel; in the others to the fuels as they stand.

<sup>2</sup> In these analyses the numbers in the *Coke* column represent fixed carbon (coke minus ash).

TABLE XXXIX (continued)

Compositions of Different Coals

[illegible]

ating coke, obtained as a secondary product in the manufacturing gas from long-flame bituminous coal, forms more highly porous lumps of a grey colour. Metallurgical coke, made from a fat, short-flame coal, is resistant, sonorous and has a metallic lustre. In every case, coke consists, apart from a small amount, of carbon.

\*  
\* \*

Coke should contain only 1-2% of moisture; if washed and air-dried it should contain as much as 5-6%. With certain cokes the ash may amount to 10-15% and good samples usually contain 4-10%.

Coke usually contains 83-90% C, 0.3-2% H, 2-6% O and 1-2% S. The amount of sulphur may reach 2.5%, but for metallurgical coke the limit is that it shall not exceed 1%. With cokes not excessively rich in sulphur the calorific power varies from 7000 to 8000 calories.

It is required that a good metallurgical coke should not contain more than 10% of water, 8% of ash and 0.5% of sulphur, and that its calorific value should be about 8000 cal.

## AGGLOMERATED FUELS

### (Briquettes)

The quality of the coal and agglutinating material used is of great importance. Bituminous coal is the more commonly employed material, but it is often taken to act as cohesive, although many other materials are used.

Briquettes are usually brick-shaped, but cylinders, sometimes perforated to facilitate access of air, and ovoid forms are also made.

In the determination of the calorific value of these fuels, in addition to the determinations given under the general methods, it is important to ascertain the *cohesion* or *strength* of the briquette. This may be done with a special apparatus, or by a crushing test in which the largest face (with brick-shaped briquettes).

Also the *resistance to heat* is tested, in order to find out how long the briquette is softened when kept for a certain time at a definite temperature (usually at 60°).

The *determination of the pitch* used as agglutinant may be carried out by extraction in a Soxhlet apparatus with carbon disulphide. The residue ceases to become coloured (this usually requires at least 24 hours) and after evaporating the carbon disulphide and weighing the residue the weight of the pitch is determined.

to that of the good coal from which they are made and in general should not be below 7500 cal.

## CHAPTER VII

# COAL TAR

## AND ITS PRODUCTS

dry distillation of coal, as in the manufacture of illuminating gas, the preparation of coke, *crude tar* is collected as a secondary product. When subjected to further treatment this gives, on distillation, a series of products being distinguished according to the temperature at which they are distilled, as *light*, *medium*, *heavy* and *anthracene oils*. The residue left after distillation is *pitch*. From the light oils are obtained, by further distillation, *benzene* (benzole) and the *toluenes* (toluoles), which are used in the explosive industries and as solvents. The medium, heavy and anthracene oils yield other products of industrial importance, such as *naphthalene*, *anthracene*, *carbolic acid*, *pyridine bases* and *impregnating oils*. The products are considered separately in succeeding paragraphs, the method of preparation being made in each case being indicated.

—With very viscous liquids, such as crude tar and heavy oils, it is not easy to obtain a sample exactly representing the composition of the whole mass. To take such a sample from the bottom of a vessel containing the material, use is made of a metallic dipping cylinder, 1 in. wide and closed at the bottom by a plug which is raised and lowered by means of an iron wire passing through the cylinder itself. The cylinder is filled several times and all the samples mixed so as to obtain a representative sample as possible. With a non-viscous liquid, however, it is easy to mix the mass before extracting the sample.

For products such as naphthalene and anthracene, the mass is divided into portions to see if it is all of the same appearance, and samples are taken from different parts and mixed before analysis.

## CRUDE TAR

Crude tar is a dense, black, oily liquid with a characteristic odour due to the presence of aromatic hydrocarbons, phenols, naphthalene and pyridine. When it is to be distilled, the tests made are 1-4 (below), but if it is to be used as fuel, the ash content and the calorific power are determined for the light oils (*q.v.*).

**Distillation of the Water.**—Since tar exhibits a tendency to emulsify, it is better present to separate, either the sample should be taken

subsequent determination being scarcely necessary.

In a glass or copper distillation flask, a weighed quantity of 100 of the well-mixed sample is distilled with 50 c.c. of benzene (90% and through a condenser. The distillation is carried up to 190° in about an hour, the distillate being collected in a graduated cylinder and the volume of the aqueous layer read off. Industrially, the water is determined during the distillation test and is collected with the light oils, from which it separates on standing, so that it may be easily measured.

**2. Determination of the Specific Gravity.**—The tar is first completely freed from water. To this end it is left for 24 hours in a closed vessel in a bath of water heated to a temperature not higher than 50°, being stirred from time to time to facilitate the rising of the drops of water and the escape of bubbles. When the layer of water is thoroughly separated, it is decanted or siphoned off and the specific gravity of the residual tar determined at 15° C. With a fairly mobile tar, an ordinary densimeter or picnometer may be used, but with very dense tar either a picnometer for solids, with a ground stopper surmounted by a tube with a mark on it, or an ordinary weighing bottle with a rill in the stopper<sup>1</sup> may be used.

**3. Determination of the Free Carbon.**—According to Kopp's method,<sup>2</sup> 10 grams of the tar are boiled with 25 c.c. of acetic acid and 25 c.c. of toluene in a conical flask with a reflux apparatus and the hot liquid filtered through two filter-papers reduced to equal weight and placed one inside the other. The residue on the filter is washed with hot toluene and the latter passes through colourless, the two filters being then separated and dried at about 120° until of constant weight. The difference in weight between the two filters gives the free carbon.

From the content of free carbon (*c*) thus obtained, the yield of pitch of a definite hardness may be determined—knowing the proportion *k*, of free carbon in the pitch—by the formula  $x = \frac{100c}{k}$ .

Assuming that, for a good pitch of medium hardness, *k* is 28%, a tar containing *c*% of free carbon will give  $x = (100c \div 28)\%$  of such pitch.

**4. Fractional Distillation.**—Fractional distillation of tar presents difficulties on account of the bumping, which is due mainly to the presence of water. It is, therefore, necessary first to dehydrate the tar as completely as possible in the manner indicated above, then to distil from a flask more than half full and to heat with great care until all the residual water is eliminated. The apparatus used for the distillation of mineral oils may be employed (see Chapter VIII). It is also advantageous to pass through the boiling liquid a gentle current of air by means of a capillary tube connected with the atmosphere.

ing over, become intensely red. The residue in the retort, the pitch, is weighed.

The distillation test is carried out on larger quantities (0.5 to 10 g.) in a metallic vessel, so that results in greater accord with those of the small test obtained.<sup>1</sup>

\* \* \*

Specific gravity of coal tar (dry) usually varies from 1.100 to 1.280, but values may be below 1. The composition of the tar varies according to the yield of the coal yielding it and to the mode of heating (whether in retorts or in horizontal retorts), and similar variation is shown by the yield of products. Tar contains 10–35% of free carbon and the quantity of volatile matter in it when sold to the distilleries is 4–5%.

## CRUDE LIGHT TAR OILS

Analysis of these products includes the following determinations:

**Determination of the Specific Gravity.**—By means of a hydrostatic balance at 15° C.

**Distillation.**—100 c.c. are fractionally distilled from a glass retort or a copper vessel of 150 c.c. capacity, furnished with a thermometer and connected with a condenser. The portion passing over up to 120° is crude benzole (with toluole, etc.) and that between 120° and 180° is crude naphtha (*solvent naphtha*); the residue is regarded as middle oils. The crude benzole may be tested by the reactions for detecting the presence of petroleum oils (benzine) or oil of turpentine (*see later*: Benzole, Oil of Turpentine, Vol. II).

**Determination of the Phenols.**—The fractions obtained from the distillation are reunited, the containing vessels being rinsed with water, and the whole introduced into a 500 c.c. graduated cylinder with a stopper and repeatedly shaken with 100 c.c. of caustic soda solution (2%). After being left at rest for some time, the volume of the liquid underneath is read, the increase in its volume giving the amount of phenols by volume.

For the exact determination the alkaline layer is collected and washed with water in a water-bath until addition of water no longer produces a precipitate. When cold, the liquid is acidified with hydrochloric acid and sodium chloride, the layer of phenols which separates being

**Determination of the Bases.**—The oil freed from phenols by the method described is repeatedly shaken with 30 c.c. of 20% sulphuric



giving the percentage by volume of the bases. These may also be determined directly by collecting the acid liquid, carefully adding to it excess of caustic soda solution (D 1.40), and measuring the bases separate.

\* \* \*

The specific gravity of the light oils usually lies between 0.900 and 0.930; they contain 5-15% of phenols and 1-3% of bases.

## MIDDLE AND HEAVY TAR OILS

With these the following determinations are made :

1. **Determination of the Specific Gravity.**—As with light oils.
2. **Distillation.**—This is carried out either with the product free from naphthalene, which is distilled from a flask with a long side-tube but no condenser (to prevent crystallisation of naphthalene), or with the product free from naphthalene, or with that free also from phenols and bases, resulting in determinations 3 and 4.

3. **Determination of the Crude Naphthalene.**—From 0.5 to 1.0 g of the oil is left for 24 hours at 15° and then cooled if necessary to 0°; the naphthalene to crystallise, this being pumped off on a cloth or filter, pressed in a press until all the oily part is removed and weighed. This represents the crude naphthalene, of which the melting and boiling points may be determined.

4. **Other Determinations.**—The oil free from naphthalene is treated with caustic soda to determine the phenols, and with dilute sulphuric acid to determine the pyridine bases, as with the light oils (3 and 4).

\* \* \*

A *good middle oil* has a specific gravity not less than 1; at least 90% distil below 260°, and it contains not less than 30% of crude naphthalene (210-220°). The naphthalene-free oil has the specific gravity 0.99-1.0 and contains 25-35% of phenols (about one-third of this being carbolic acid) and about 5% of bases.

The *heavy oils* have a mean specific gravity 1.04 and distil between 260° and 300°; they contain mainly naphthalene and other solid hydrocarbons together with 8-10% of phenols (principally cresols and higher homologues) and about 6% of pyridine bases.

## ANTHRACENE OILS

The analysis of anthracene oils includes, besides determinations of specific gravity and of the behaviour on distillation—which are carried out as with the middle oils—only the determination of the anthracene

...ation of the Free Carbon.—As with tar (*see* Crude Tar,

**Combustion of the Ash.**—2 or 3 grams of the pitch are burnt crucible in a muffle and the residue weighed.

**Combustion of the Volatile Matter and Coke.**—As with fuels important to note the appearance of the coke—whether swollen, cracked.

**Softening and Melting Temperatures.**—These serve better than indicate the degree of purity of the pitch. In a beaker of water about half a litre of water is suspended a cube of the pitch on one side or a disc 4–5 mm. thick at the end of an iron wire, 5 cm. from the bottom. A thermometer is immersed with its bulb at the same depth as the pitch and the temperature of the water is noted minute. From time to time the pitch is withdrawn to ascertain its consistency when pressed between the fingers. The *temperature of softening* is taken as the lowest at which the pitch can be twisted between the fingers, while the *temperature of softening* is that at which it can be bent between the fingers without force and the *melting point* as that at which it begins to drop.

**Comparison of the Characters of Tar Pitch, other Pitches and Natural Bitumen.**—The characters of these products are as follows :

Vegetable Pitch (Black or Marine Pitch).	Petroleum Pitch.	Stearine Pitch.	Natural Bitumen.
Black, with an odour recalling that of vegetable tar.	Black, almost odourless.	Black, odour of fatty substances.	Blackish, usually solid and hard, sometimes soft.
Very soluble in alcohol, giving a brown solution containing resinous matters and giving the reactions for phenols. It colours potash solution brown.	Almost completely insoluble in petroleum ether.	Insoluble in alcohol and partially soluble in petroleum ether.	Insoluble in alcohol; does not give the reactions for phenols.
The distillate has an acid reaction.	In general has no saponification number.	Has a saponification number and an acid number.	

carbon content is rarely less than 25–30%, and for that from vertical retorts or blast-furnaces, 5–7%. The ash content is less than 0.5% for gas pitch and more than 1% (6–10%) for that from blast-furnaces. The yield of coke varies from 30 to 60%, and the coke has a more or less porous appearance according to the type of pitch from which it is derived (very porous with the very hard pitches, less so with the others).

As regards the temperatures of softening and fusion, the following limits may be taken for different types of pitch:

*Soft*: Softens at 40°, melts at 50–60°.

*Hard*: Softens at 60°, melts at 70–80°.

*Very hard*: Softens at 80–85°, melts at 90–120°.

A good pitch for making briquettes should, according to Spilker<sup>1</sup> have the following properties: not more than 0.5% of ash; softening point between 60° and 75°; solubility in aniline, 70–75%, and in carbon disulphide, not less than 70%; yield of coke, 45%; appearance of coke, caking and not too much swollen.

## IMPREGNATING OILS

These are usually creosote oils or anthracene oils, freed more or less completely from crystallisable substances, and are used for the impregnation of wood, especially railway sleepers and telegraph poles, with the object of preserving it.

In general they are brownish red or blackish liquids, more or less fluorescent, somewhat viscous, and with a more or less marked odour of the products of tar distillation.

The principal tests to be made are:

**1. Determination of the Specific Gravity.**—By means of a hydrometer or Westphal balance at 15° C.

In some cases measurements are made at higher temperatures, e.g., at 25, 45, 50° C.; the temperature used must be indicated in the report.

**2. Distillation.**—This is carried out in a tubulated retort of about 300 c.c. capacity, furnished with a thermometer. The retort is charged with 100 c.c. of the liquid and the thermometer bulb arranged at about 2 cm. from the liquid, which is heated so that 120 drops per minute pass over; the different fractions are measured.

**3. Determination of the Phenols and the Naphthalene.**—The fractions obtained as under 2 are reunited in a graduated cylinder, shaken repeatedly with 100 c.c. of caustic soda solution (D 1.15) saturated with sodium chloride and then left to settle; the increase in volume of the soda solution gives the percentage of phenols. In the supernatant oily layer the naphthalene is determined by cooling (to 15°) in the manner indicated

may also be required; these are ascertained as with heavy  
see these: Chapter VIII).

\*  
\* \*

position of impregnating oils varies according to the conditions of  
Thus, a specific gravity of 1.03–1.10 or of 1.05 at 50° is required :  
30% of naphthalene ; a content in phenols of 5–10%, and various

## BENZOLES

l benzoles from the tar industry are mixtures in varying  
benzene, toluene and xylenes, and contain also ethylbenzene,  
enes and other homologues of benzene. The separate pure  
are obtained by  
complicated rectifica-

ed benzoles are colour-  
liquids with a character-  
odour ; any turbidity  
ence of water.

and determinations to

**etermination of the  
vity.**—By the West-  
densimeter or picno-

**ation.** — This test,  
to characterise com-  
ples, may be carried  
inary distillation flask,  
t used for light mineral  
ially, however, the de-  
ctions given by Krae-  
ker<sup>2</sup> are followed, so  
able results may be

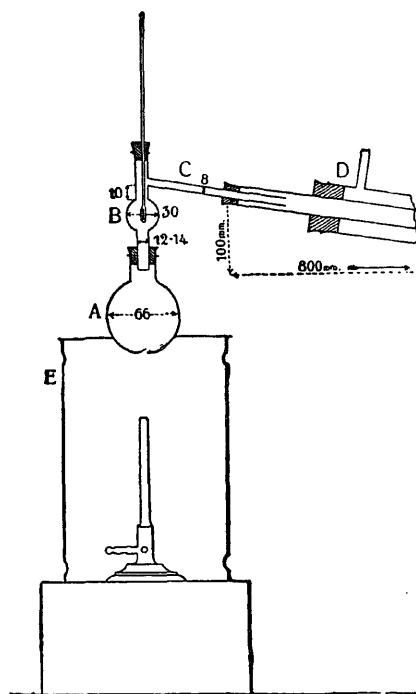


FIG. 37

ation apparatus used is

Fig. 37 and consists of a copper vessel A, 0.6–0.7 mm. thick,  
in capacity and of the dimensions indicated. To the mouth  
is fitted a dephlegmator B, 14 mm. wide and 150 mm. long,  
a bulb and with a side-tube 8 mm in diameter fixed almost

The lateral tube of the dephlegmator is connected with a condenser *D*, 800 mm. long, inclined so that the top end is 100 mm. higher than the free end.

With this apparatus 100 c.c. of the liquid are distilled in such a manner that 5 c.c. distil over per minute (2 drops per second), fractions passing over at different temperatures (up to 100°, 120°, 145°, 160°, 175°, 190°, according to the different types of benzole) being collected in a graduated cylinder and measured.

For exact determinations it is necessary to take account of the atmospheric pressure, bearing in mind that for pressures between 720 and 780 mm. the percentages given by the distillation should be diminished by 0.033 for 90% benzoles and by 0.077 for 50% benzoles for each millimetre of pressure below the normal pressure of 760 mm. and increased by the same amounts for each millimetre above 760 mm.

**3. Determinations of the Separate Hydrocarbons.**—To separate and estimate approximately the different hydrocarbons contained in commercial benzole, the latter must be fractionally distilled in a manner rather different from that just described, a moderately large amount of substance being treated in an apparatus furnished with an efficient dephlegmator. Use is generally made of a copper vessel of the form and dimensions indicated (in millimetres) in Fig. 38, a six-bulb Le Bel-Henninger fractionator, 60 cm. long, being fitted to it. The fractionator is provided with a thermometer and joined to a condenser, and 1 kilo of the product is distilled at the same rate as in 2 (above), the different fractions being collected in tared receivers, which are subsequently reweighed.

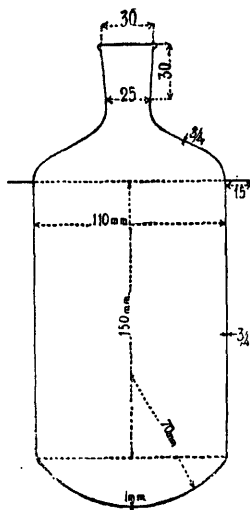


FIG. 38

The separation of the different hydrocarbons may be effected by further fractional distillations, regard being paid to the boiling points, which are as follows: benzole, 80–81°; toluole, 110–111°; xyloles, 138–142° (*o*-xylene, 142°; *m*-xylene, 139–140°; *p*-xylene, 138–139°); ethylbenzene, 137°; trimethylbenzenes, 163–175°.

The fractionation of the different commercial products is carried out on the basis of the following temperature limits:

	Benzole (50% and 90%):	Pure commercial Benzole.	Toluole.	Xyloles.
First fraction	up to 79°	up to 79°	up to 109°	up to 135°
Benzole	79–85	79–81		
Intermediate fraction	85–105			

ted by means of fractional distillation, their boiling points being the respective quantities may, however, be determined approxi-  
arding the distillate between  $135^{\circ}$  and  $137^{\circ}$  as *p*-xylene, that  
nd  $140^{\circ}$  as *m*-xylene, and that between  $140^{\circ}$  and  $145^{\circ}$  as *o*-xylene ;  
er to uncorrected temperatures, i.e., those indicated by a ther-  
its scale only partially immersed in the vapour.

**on and Estimation of Impurities.**—The impurities of  
enzoles are principally carbon disulphide, thiophene, paraffin  
and naphthalene.

**DISULPHIDE.** This is *detected* by shaking about 10 c.c. of  
better, of the first fractions of its distillate, with 5 or 6 drops  
azine and leaving the mixture at rest for an hour. In presence  
2% of carbon disulphide, a white precipitate of phenylhydra-  
phocarbazine is formed.

*termination*, the ammonium xanthate (Hoffmann) reaction is

of 50 grams of the benzole with 50 grams of alcoholic potash  
rams of KOH in 90 grams of absolute alcohol) is left for some  
rdinary temperature and is then shaken with 100 c.c. of water.  
layer is separated from the benzole, which is washed two or  
ith water, the total aqueous liquid being made up to 400 c.c.  
n, or an aliquot part of it, the potassium xanthate formed is  
olumetrically by means of a standard copper solution (12.468  
tallised copper sulphate per litre).

ected by acidifying the aqueous liquid containing the xanthate  
acid and then adding the copper sulphate solution until the  
xcess, i.e., until a drop of the liquid gives the brown coloration  
m ferrocyanide. The number of c.c. used, multiplied by  
the percentage of  $\text{CS}_2$  in the aqueous liquid and from this the  
the benzole may be calculated.

**THIOPHENE.** This is *detected* by the indophenine reaction. To a  
of isatin in a porcelain basin, a few c.c. of pure conc. sulphuric  
d and then the benzole, the liquid being covered with a clock-  
to itself for some hours : in presence of thiophene, blue rings  
the isatin granules.

oles guaranteed free from thiophene are tested for the latter.

**FIN HYDROCARBONS (benzines).** These are *determined* by  
the benzoles into the soluble sulpho-acids (Kraemer and Spil-  
rams of the benzole are shaken for 15 minutes in a separating

For exact determinations, the hydrocarbons remaining suspended in the sulphuric acids employed should be collected. The acid liquors are poured slowly and with shaking on to an equal weight of pounded ice in a flask, the temperature never exceeding  $40^{\circ}$ . The liquid thus obtained is distilled and the oil separating at the surface of the first 50 c.c. of distillate added to the quantity determined directly. The total oil thus obtained is repeatedly purified with fuming sulphuric acid (20% of anhydride) in lots of 30 grams each until no further diminution in volume takes place. It is then washed with water and measured, the volume, divided by 2, giving the quantity of paraffin hydrocarbons in 100 of the benzole.

(d) NAPHTHALENE. 10 c.c. of the benzole are allowed to evaporate spontaneously in a glass dish, any naphthalene present remaining crystallised on the walls of the dish.

**5. Degree of Refining.**—Benzoles may contain larger or smaller quantities of resinous substances not completely removed by refining. The presence of these substances may be detected as follows :

(a) WITH SULPHURIC ACID. 5 c.c. are added to 5 c.c. of conc. sulphuric acid in a cylinder with a ground stopper, the mixture being shaken for two or three minutes and the colour of the acid observed. Pure products do not colour the acid at all, and commercial products colour it pale yellow or brown according to the extent to which refining has been carried. The coloration may be measured by comparison with solutions of potassium dichromate in sulphuric acid.

(b) WITH BROMINE. 5 c.c. of the benzole are mixed in a beaker with 10 c.c. of dilute sulphuric acid (1:5) and a decinormal potassium bromide and bromate solution (9.9167 grams KBr + 2.7833 grams  $\text{KBrO}_3$  per litre) run in, slowly and with shaking, at intervals of five minutes until the bromine liberated no longer undergoes absorption; this is shown by the orange-yellow coloration of the benzole and by the blue colour imparted to starch-iodide paper. The degree of refining is in inverse ratio to the amount of bromine absorbed (1 c.c. N/10-solution = 0.008 gram Br). The loss during further refining will be 1% per 0.2 c.c. of the bromine solution used.

\*  
\* \*

The benzoles most commonly found on the market may come from the distillation of light tar oils or from the distillation of the washing oils obtained by exhaustion of the gas from the manufacture of coke or coal gas by means of heavy oils. These are mixtures in varying proportions of benzene and higher homologues. Examples of the more important characters of these products

TABLE XL

## Character and Composition of Benzoles

	Specific Gravity at 15° C.	Percentage of Distillate at different temperatures.	Composition.			
			Benzole.	Toluole.	Xyloles.	Higher homologues.
.	0.880-0.883	90-93% up to 100°	84	13	3	—
.	0.875-0.877	50-53% up to 100° 90-93% up to 120°	43	46	11	—
.	0.870-0.872	90% at 100-120°	15	75	10	—
.	0.872-0.876	90% at 120-145°	—	25	70	5
(a).	0.874-0.880	90% at 130-160°	—	5	70	25
.	0.890-0.910	90% at 145-175°	—	—	35	65
.	0.920-0.945	90% at 160-190°	—	—	5	95

contain varying proportions of impurities. Thus, thiophene in the earlier of the above marks and carbon disulphide occurs 2-1% in benzole I and 0-0.5% in benzole II, whilst it is usually exceeding marks. In marks I, II and III, the amount of paraffin is at most 1%, and in other marks rather more. Pure benzoles give a white precipitate with 1 c.c. of the bromide-bromate solution, but the commercial benzoles give a precipitate of 0.6-1%.

The behaviour of the principal commercial products on fractional distillation in a rectifier for the separation of the individual hydrocarbons is as follows: the following serve as examples:

	Benzole I.	Benzole II.	Pure com- mercial Benzole.	Com- mercial Toluole.	Com- mercial Xylole.
.	1.0%	0.3%	0.5%	0.3%	1.3%
.	78.8%	18.3%	98.0%		
tion .	10.0%	47.5%	1.5%		
.	8.0%	23.7%		97.3%	
.	2.2%	10.2%	2.4%	96.5%	
es, etc.					2.2%

of the three isomerides in commercial xylole are about 1% of *p*- and 5 of *o*-xylole.



cating approximately the melting point. The fused mass is then stirred with the same thermometer until naphthalene crystals again begin to form and the column of the thermometer remains stationary for some time. This is the solidifying point, which, with pure naphthalene, corresponds with the melting point.

**2. Presence of Oily Products.**—A packet of 50 grams of the naphthalene wrapped in several thicknesses of filter-paper is subjected in a press to a pressure of about 150 atmos. for 10 minutes, the paper being then examined to see if it is stained by the oil absorbed.

**3. Behaviour towards Petroleum Ether.**—2 grams of the naphthalene are treated in a test-tube with light petrolcum to see if a clear, colourless solution is obtained.

**4. Behaviour towards Sulphuric Acid.**—4 grams are heated in a test-tube in a water-bath with 4 grams of conc. sulphuric acid until a clear solution is obtained, the colour being observed. The sulphuric acid solution is poured into about 40 c.c. of water to ascertain if the whole remains clear and colourless.

**5. Stability towards Light.**—2 grams of the naphthalene on a clock-glass are left for 1–2 hours in a desiccator over conc. nitric acid (not fuming), the naphthalene being then examined to see if it has remained unaltered or if it is coloured.

\* \*  
\* \*

*Pure* commercial naphthalene is white or slightly yellow and melts at 79.6–79.8°; it should not mark paper (test 2) and should volatilise completely if heated on a water-bath; test 3 should yield a clear solution, at most pink or reddish, which should remain clear on dilution; it should dissolve completely in petroleum ether (test 4) and should remain unchanged when subjected to test 5 (slightly impure naphthalene becomes pale pink).

## ANTHRACENE

Commercial anthracene is always impure, containing principally naphthalene, methylanthracene, carbazole, paraffin wax, phenanthrene, etc. The technical examination of crude anthracene is limited to the determination of the anthracene content and to tests for the presence of impurities which are harmful in the coal-tar colour industry.

**1. Determination of the Anthracene.**—Luck's method, based on the oxidation of anthracene to anthraquinone by means of chromic acid, is usually employed. In a flask with a capacity of about half a litre, fitted with a tapped funnel and a reflux condenser, a boiling solution of 1 gram of the anthracene in 45 c.c. of glacial acetic acid is treated with a solution

tion and finally with boiling water until the alkalinity contents of the filter are washed by means of a fine water porcelain dish, the water being evaporated and the residue heated for 10 minutes on a boiling water-bath with 10 per cent. sulphuric acid (D 1.88). The dish is subsequently left in a desiccator for 24 hours, the contents diluted with 200 c.c. of cold water, the anthraquinone filtered, washed as before, placed in a desiccator, dried at 100° and weighed. For greater exactness the water is evaporated and the residual ash determined: anthracene = anthracene.

**of Impurities.**—Among the more common impurities found in certain applications of crude anthracene, e.g., in the manufacture of carbazone, are methylantracene, carbazole, paraffin wax, etc. These substances are detected as described in the following paragraphs; for their quantitative determination, which is rarely required and for special purposes, special works must be consulted.

**ANTHRACENE.** When anthracene containing methylantracene is treated with chromic acid, as described above, methylantracene forms threads variously twisted rather than needles. Methylantracene is distinguished from the latter by its solubility in benzene.

**Carbazole.** The anthracene is extracted with ethyl acetate, the extract dried, and the residue treated with a few drops of ethyl acetate. Some drops of nitrobenzene and a little phenanthrene are added. The presence of carbazole is shown by the formation of small, copper-coloured crystals.

**Paraffin.** 10 grams of anthracene are treated with 100 c.c. of ether. The etheral solution separated and evaporated and the residue heated with 10 grams of fuming sulphuric acid (20% of anhydride) for 10 minutes. The whole is poured into 500 c.c. of water and, after the paraffin wax separated at the surface is filtered off, washed with water, the filter allowed to dry and then moistened with alcohol, the paraffin collected by adding ether. The etheral solution thus separated, and the residue, dried at 105°, gives the solid paraffin.

**Phenanthrene.** A certain quantity (1 kilo) of the product to be purified is dissolved in the hot with double its volume of toluene. After the dissolved anthracene and carbazole are separated and the toluene distilled, the portion passing over between 300° and 340°—the greater part of the phenanthrene being collected—is redistilled.

states with an odour resembling that of sulphuric acid, according to the degree of purification, it contains 30–39% of anthracene (English anthracene A contains 40–50 %).

*Pure anthracene* forms white, tabular crystals with a blue fluorescence, m.pt.  $216.5^{\circ}$ , b.pt.  $360^{\circ}$ ; it is slightly soluble in alcohol, ether, benzine, carbon disulphide and cold benzene, and readily soluble in the hot in benzene, pyridine and glacial acetic acid.

## CARBOLIC ACID

*Crude* and *pure* carbolic acid are on the market. The former is of somewhat variable composition, the name being often given to yellowish or dark brown carbolic oils containing, besides varying quantities of neutral tar oils, also phenol and its homologues (mainly cresols), whereas it is also used to designate pale red products rich in phenols and crystallising more or less easily when cooled. The pure product is colourless or pale red, crystallisable and soluble in 15 parts of water.

In very impure products the determination of the phenols and neutral oils is carried out as in 2; in the others, the water, solidification point, and the solubility are determined (3, 4 and 5) and, if required, the quantitative estimation according to Koppeschaar (*see* 2).

**1. Characteristic Reactions of the Phenols.**—The following reactions are used:

(a) The aqueous solution of a phenol gives a violet coloration with dilute ferric chloride solution (provided mineral and organic acids, alcohol, ether and glycerine are absent).

(b) When heated gently with a little ammonia and a few drops of sodium hypochlorite, the aqueous solution of a phenol gives an intensely blue coloration.

(c) The substance is shaken with water and the aqueous solution treated with bromine water: if it is a phenol, a voluminous, white precipitate of tribromophenol, at first flocculent and afterwards crystalline, is produced. It is soluble in alkali and is reprecipitated on acidification of the alkaline solution. The tribromophenol reaction (*Landolt's reaction*) is sensitive to about 1 part in 44,000. The cresols and also other organic compounds are precipitated by bromine water.

(d) A very sensitive reaction is as follows: About 1 c.c. of the oil to be examined is shaken with 1 c.c. of alcohol, after which 2 c.c. of water and 1 c.c. of about 1% nitrazole solution (fresh) are added and again shaken: addition of a little caustic potash then colours the aqueous layer an intense red in presence of phenols.

**2. Determination of Phenols and Neutral Oils.**—The approximate

## CARBOLIC ACID

it to dilute the sample with an equal volume of ligroin, the water being then subtracted from that of the neutral oils sample. For control, the alkaline layer may be separated, acidified in a flask, and the volume of the phenols separating read.

For exact results are obtained as follows: 120 grams of the sample examined are distilled until only about 8 grams of residue remain in the flask, the distillate being dissolved in ether and shaken in a separating funnel with 10% caustic soda solution. The total solution is washed several times with ether and then acidified with hydrochloric acid diluted with an equal volume of water, the acid layer being extracted repeatedly with ether in a separating funnel to remove the phenols. The ethereal solution of the latter is washed with water and placed in a weighed flask, almost all the ether being distilled off. The flask is then closed by a stopper through which passes a vertical tube with a thermometer, and the last portions of ether then evaporated. It is taken that the temperature does not exceed  $100^{\circ}$ ; the flask is re-weighed, the increase in weight representing the phenol. It is assumed that the phenol is *not accompanied* by its homologues (creosotes), which are determined volumetrically by Seubert and Beckurts' method or by van Roschaar's method:

The reagent is made of a solution of potassium bromide and potassium bromate, 5KBr + KBrO<sub>3</sub>, which in presence of an acid liberates chlorine according to the equation:  $5\text{KBr} + \text{KBrO}_3 + 6\text{HCl} = 6\text{KCl} + 3\text{Cl}_2 + 3\text{H}_2\text{O}$ . About 1 gram of the sample (or more, if poor in phenol) is dissolved in water to a litre, 25 c.c. of this solution being

while stirred with the thermometer, the solidifying point of pure mass beginning to crystallise stationary. The highest temperature point of the product tested

**5. Solubility.**—1 c.c. of with 15 c.c. of water, should be pure. The more impurities

Pure carbolic acid has the melting point,  $183-184^{\circ}$ . Products are (up to  $32^{\circ}$ ), this resulting from the cresols.

This is obtained mainly as crude or pure. *Crude pyridine* of the pyridine and quinoline bases, pyrrole and ammoniacal penetrating and peculiarly inflammable, soluble in water. In small proportions with water or in the state it is used mainly for the disinfectant. The following are the tests

**1. Colour.** The colour

thermometer with its bulb central. The flask is heated over the flame on an asbestos card in such a manner that 5 c.c. distil per minute; when the temperature reaches  $140^{\circ}$ , the heating is interrupted, the liquid is allowed to pass over being still collected and the volume of the distillate measured. The distillation is continued up to  $160^{\circ}$  and the volume of the distillate measured.

**Behaviour towards Water.**—50 c.c. of pyridine are treated with 100 c.c. of water and it is noted whether the two liquids mix completely. The solution is clear or more or less turbid. The opacity may be determined by looking through the mixture in a tube of 1 cm. diameter indicated under 1 (above) and noting the possibility or otherwise of obtaining a precipitate of definite dimensions.

**Behaviour towards Caustic Soda.**—In a graduated cylinder with stopper, 20 c.c. of the pyridine are shaken with 20 c.c. of caustic soda solution, D 1.4 (50 grams of sodium hydroxide in 100 c.c.) and left for 24 hours; the volume of the upper layer, consisting of the pyridine bases, is measured. The difference between this volume and 20 c.c. gives the percentage of bases.

**Determination of the Bases.**—10 c.c. of the pyridine are diluted with water to 100 c.c. and 10 c.c. of this solution titrated with normal sulphuric acid until a drop of the liquid produces on Congo red paper <sup>1</sup> a blue colour which quickly disappears. The result is expressed by indicating the number of c.c. of normal acid employed.

The exact determination is obtained by François' gravimetric method based on the insolubility in anhydrous ether of the additive compound of pyridine hydrochloride with gold chloride. About 0.1 gram of pyridine is weighed into a porcelain basin and treated with water, 20–30 c.c. of hydrochloric acid and excess of gold chloride solution, a precipitate is formed and the liquid remaining deep yellow. The whole is evaporated to dryness on a water-bath and, when all the hydrochloric acid is eliminated, the residue is decanted with anhydrous ether as long as any colour is still present (to eliminate the excess of gold chloride). The precipitate remaining is washed with ether, dried, and the metallic gold weighed:  $\text{Au} \times 0.401 = \text{pyridine}$  when pure pyridine is taken. With crude pyridine, the weight

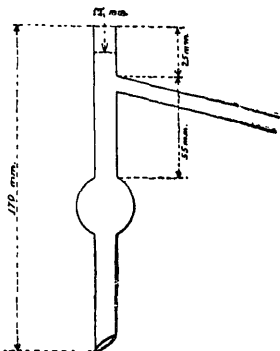


FIG. 39.

Test 6 : Analyze as pyrimidine and determine as usual. Copy at least 10 times.

Test 7 : not less than 9.5 c.c. N-sulphuric acid should be used.

## CHAPTER VIII

### MINERAL OILS

#### AND PRODUCTS DERIVED FROM THEM

*The petroleum* yields various industrial products which may be grouped following classes :

*Light oils* (gasoline and naphtha), b.pt. below  $150^{\circ}$  C.

*Lamp oil* or *kerosene*, principally the fractions boiling between  $150^{\circ}$  and  $250^{\circ}$  C.

*Medium oils* (gas oils), intermediate to lamp oil and the heavy oils.

*Heavy oils*, which include the fractions distilling above  $300-310^{\circ}$  C. and treated to render them suitable as lubricants.

*Residuum*, which consists of the residue left after distillation of the light and medium oils and sometimes also of part of the heavy oils, without further treatment.

*Asphaltes*, composed of hydrocarbons semi-solid at the ordinary temperature.

*Solid paraffin* or *paraffin wax*, formed of solid hydrocarbons.

Products analogous to these are obtained by distillation of *bituminous* rocks and are termed *shale oils* ; these also yield *light oils* (shale spirit), *gas oils*, *heavy oils*, and a considerable quantity of solid paraffin.

Similar to the last is *ceresine*, obtained by refining *ozokerite* or *earth* wax. A product of similar appearance to ozokerite is *montan wax*.

These products are treated in the following articles, together with *lubricating oils* now largely used industrially and mostly having a basis of mineral oil. In sampling these products, reference may be made to the directions given for oil or tar.

#### CRUDE PETROLEUM

It is usually a brown or blackish liquid, but sometimes reddish or yellow, with a characteristic bituminous odour ; it is often turbid owing to the presence of suspended solid substances.



should be made at 15° or referred to 15°, the mean temperature of specific gravity being 0.0007 (0.0006–0.0008) per 1°.

**2. Fractional Distillation.**—In order that concordance be obtained, this should always be carried out under certain conditions and in an apparatus of fixed dimensions. Engler's in Fig. 40, is generally used. 100 c.c. of the oil are placed in the flask which is connected with a condenser 60 cm. long and heated and the flask being protected with a sheet metal mantle.

The initial temperature of distillation is that at which the first drop of distillate issues from the condenser fitted to the side-tube. The velocity of distillation should be such that two drops fall per second. The distillate is collected in several graduated cylinders, each of single 100 c.c. cylinder in which the volumes of the distillates

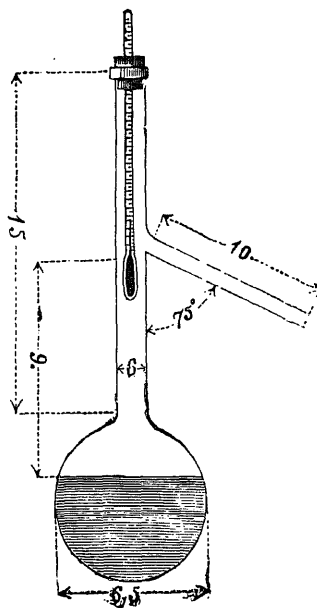


FIG. 40

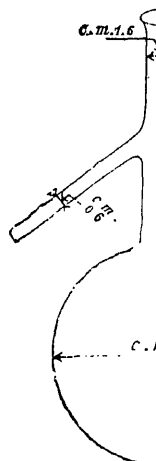


FIG.

temperatures are read off successively. The distillation is complete when the flask contains only residuum or white fumes appear. The distillates usually collected are:

Benzine: up to 150° C.

Lamp oil: 150–300°.

Heavy oils: above 300°.

height of the distillate up to  $310^{\circ}$  is determined.  
the mineral oil contains much water, it is convenient to dehydrate means of calcium chloride and to decant it before distillation in order avoid bumping during the heating.

**Flash Point.**—The *flash point* of an oil is the temperature corresponding to the initial evolution of vapour forming with air a mixture capable of igniting in contact with a flame, or, more accurately, the temperature at which such vapour can be detected under definite experimental conditions.

This determination is made with crude petroleum as with light oils (*see*

With crude petroleum poor in light oils, however, the high flash point requires the use of the apparatus employed with lamp oil or heavy oil (*see* the paragraphs concerned).

**Temperature of Ignition.**—This is the temperature at which the mineral oil, coming into contact with a flame, ignites and continues to burn. The determination, *see* Light Mineral Oils.

**Calorific Power.**—As a rule this is determined only when the crude petroleum is to be used as a fuel, as is the case with that from certain localities (e.g., California); the Mahler bomb calorimeter is used (*see* Fuels). If the petroleum is poor in light oils, 1–1.5 gram of it is weighed directly into the capsule for holding the fuel, but if rich in volatile matter it is well to put it in a small glass bulb with the ends drawn out, the igniting wire being passed through the bulb; the bulb is placed in the capsule and just before the bomb is closed the two ends are broken in order to facilitate the access of the oxygen to the liquid.

## 2. Chemical Tests

**Determination of the Water** (Marcusson's method).<sup>1</sup>—100 c.c. of the product are mixed with 50 c.c. of xylene and the mixture distilled, in the presence of a few scraps of pumice, best in an oil-bath until the water has passed over. The distillate is collected in a graduated cylinder and the volume of the lower aqueous layer measured.

**Determination of the Suspended Solid Matter.**—The oil is mixed with at least 20 times its volume of benzene (to dissolve any suspended pitch and asphalt), filtered after standing for some hours, and the residue on the filter washed with benzene, dried and weighed.

**Determination of the Sulphur.**—This may be carried out by the method of A. S. (see Fuel) or in the Mahler calorimetric bomb. With the former method, 1 gram of the mineral oil is mixed with sufficient of the carbonate of magnesia and sodium potassium carbonate to give a dry powder.

acid precipitated as barium sulphate :  $\text{BaSO}_4 \times 0.1374 = \text{S}$ .

This method is also applicable to all derivatives of crude petroleum which always gives good results.

**4. Determination of the Solid Paraffin.**—This is effected by the following method, after fractions below  $300^\circ$  have been eliminated. 100 grams of the crude petroleum are rapidly distilled, the distillate below  $300^\circ$  being collected. If the residue from the distillation is dark, as is usually the case, it also should be distilled—the thermometer and condenser having been removed—until only fixed, carbonaceous residue remains in the retort. The distillate above  $300^\circ$  (or the oil left in the flask if it is not distilled) is weighed and treated as follows in the apparatus shown in Fig. 42.

This consists of a vessel surrounded by felt and containing a freezing mixture in which are immersed the tube and funnel. The test material and the funnel used for the test are placed in the funnel; the funnel is connected with a pump flask. The pump flask is provided with another tube (5) which leads into the freezing mixture, through which the water from the freezing mixture can run off.

Of the oil distilled as described above, 10 c.c. are placed in a wide test-tube and dissolved in an equal volume of a mixture of absolute alcohol and ether. The test-tube is placed in the freezing mixture so as to keep it at about  $-20^\circ$ . The mixture is stirred while the liquid is stirred with the thermometer. The alcohol-ether mixture is added until the oily residue separates and only the solid paraffin remains out of solution. The liquid is then filtered through a filter, the means of a pump on the funnel kept below  $-20^\circ$ , the residue being washed

with alcohol-ether mixture (if the solid paraffin is soft, it is well washed with a mixture of 2 parts of alcohol and one of ether) until a few c.c. of the liquid leave no appreciable oily residue on evaporation. The solid paraffin is then dissolved on the filter in hot benzene into a dish, the benzene being evaporated on a water-bath—which boils vigorously—and the dish dried for 15 minutes at  $105^\circ$ , removed to a desiccator and weighed. The percentage of solid paraffin in the oil is then calculated.

By this method, a small quantity of solid paraffin remains undissolved in the alcohol-ether mixture; the result obtained should, therefore, be corrected for the small amount of solid paraffin which is

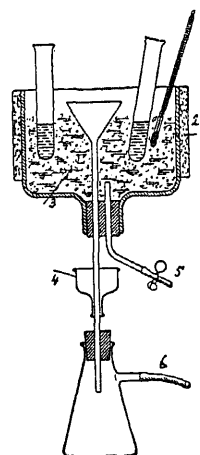


FIG. 42

in a test-tube with 20 c.c. of petroleum ether (D not above 0.7) and left overnight; any hard asphalt present is deposited in blackish flocks soluble in benzene.

(b) *Soft asphalt*. About 0.5 gram of the oil is dissolved in a test-tube in 15 c.c. of ether and the liquid treated with 7.5 c.c. of 96% alcohol; any soft asphalt present is precipitated in the form of flocks, which unite to a viscous mass adherent to the walls of the tube and soluble in benzene.

2. QUANTITATIVE DETERMINATION. (a) *Hard asphalt*. About 5 grams (or more, with a product poor in asphalt) of the oil are shaken in a litre flask with 200 c.c. of the petroleum ether used for the qualitative test and left at rest for a day. The liquid is then decanted on to a pleated filter, to which also the insoluble substances are transferred, flask and filter being washed with benzine until a few drops of the filtrate leave no oily residue on evaporation. The insoluble residue on the filter is at once dissolved in hot benzene, the solvent evaporated in a tared dish and the residue dried at 105° and, when cold, weighed.

(b) *Soft asphalt*. 5 grams of the product are dissolved, in a bottle fitted with a ground stopper and of about 300 c.c. capacity, in 25 volumes of ether, 12.5 volumes of 96% alcohol being run in to the solution, drop by drop and with shaking, from a burette. After standing for 5 hours at 15°, the liquid is filtered and the bottle and filter washed with the alcohol-ether mixture (1 : 2) until the washing liquid leaves no oily residue, or at most traces of pitchy substances, on evaporation.

The precipitate, which may contain solid paraffin as well as asphalt, is dissolved in benzene, the solution evaporated, the residue treated repeatedly in the hot with 96% alcohol (about 30 c.c.) until the alcoholic extracts no longer deposit solid paraffin on cooling. The residue, consisting only of the soft asphalt, is dried for 15 minutes at 105° and weighed.

For precipitating the asphalt in mineral oils, besides benzine and alcohol-ether, also butanone,<sup>1</sup> amyl alcohol and ethyl acetate have been proposed.

Different solvents precipitate asphaltic substances in different quantities and of different qualities, so that the analytical results are only relative and not absolute.

**6. Behaviour towards Concentrated Sulphuric Acid.**—Concentrated sulphuric acid precipitates from crude petroleum asphaltic and pitchy substances in larger or smaller quantity. In many cases it is, therefore, useful to determine these substances, this being done in the following manner.

In a graduated cylinder with a ground stopper 20 c.c. of the oil are dissolved in 80 c.c. of petroleum ether (D 0.700, and ascertained by preliminary trial to be unattacked by conc. sulphuric acid), the solution obtained

rich in middle fractions, and their heavy ones contain solid paraffin. Petroleum fractions are usually richer in light and middle than in heavy fractions.

The *flash point* is mostly near  $0^{\circ}$ , but varies with the content of volatile fractions.

The *sulphur* content is generally low (less than 1%), but in some cases it is as high as 10%. In Texan and Californian petroleum, more is found (4–5%).

The *calorific power* of crude petroleum is as a rule 10,000–11,000 B.T.U. per lb. It diminishes as the specific gravity increases. Petroleum fractions poor in volatile fractions are more particularly used directly as fuels, e.g., those of California and Mexico; petroleum with little sulphur are preferable for internal combustion engines, but those with larger proportions may also be used.

## LIGHT MINERAL OILS

### (Benzine)

These are volatile, mobile, colourless, or pale yellow liquids, which are usually clear but sometimes opalescent, in which case the presence of water or other impurities may be suspected.

The following tests and determinations are made:

**1. Determination of the Specific Gravity.**—This is made by the methods indicated for crude petroleum.

For fiscal purposes the Italian Customs authorities use two types of aerometers, one for the densities 0.610–0.700 and the other for 0.700–0.860. By means of tables published on the authority of the Ministry of Agriculture, density readings made at other temperatures are reduced to  $15.6^{\circ}\text{C}$ . If the weight of any consignment is known, the volume can then be calculated.

Besides as a means of characterising the various products contained in the name light petroleum oils, the specific gravity may serve as a test for the presence of benzoles, oil of turpentine or light resin oils, all of which have much higher specific gravities—0.86 or more.

**2. Distillation.**—Use is made of the flask already described for crude petroleum, this being connected with a good condenser and placed in a sand-bath with a lamp the flame of which is completely enclosed in a gauze cage, so that ignition of the vapours in case the flask should become overheated may be avoided.

The temperature at which the distillation commences is noted, and the distillate collected either in a graduated cylinder, the volume being observed, or in a separate tared vessel for each fraction, which is being afterwards reweighed. If the whole of the liquid does not pass over below  $150^{\circ}$ , the distillation is stopped at this temperature and the residue in the flask weighed.

a mask suspended by a dephlegmator may be used.

With very light, rectified oils, it is useful to evaporate a portion on the water-bath to ascertain if any residue remains, or to allow a little to evaporate spontaneously on a filter-paper to see if any oily spot is left.

Where exact results are required, allowance must be made for the atmospheric pressure when this varies by as much as  $\pm 5$  mm. from the normal (760 mm.).

**3. Flash Point.**—For this purpose use is made of the inner vessel *A* of the Abel apparatus (*see* Lamp Oil, Physical Tests, 4), this being placed in a metal vessel about 6 cm. high and 9 cm. in diameter containing alcohol; this vessel, in its turn, is placed in a larger metal vessel, also containing alcohol and surrounded with felt. Solid carbon dioxide is introduced into the alcohol until the temperature in the liquid to be examined reaches  $-50^{\circ}$  or  $-60^{\circ}$ ; the temperature is then allowed to rise slowly and the observations begun as with lamp oil.

This determination is seldom made, as it is known that naphtha has a low flash point, which is generally far below  $0^{\circ}$ , although with some of the heavier types it may be slightly above  $0^{\circ}$ .

**4. Temperature of Ignition.**—After the flash point has been determined, the cover of the vessel *A* is removed and for every  $0.5^{\circ}$  rise of temperature a flame is brought near to the surface of the liquid. The temperature of ignition is taken as that at which persistent combustion of the liquid itself takes place.

This determination also is rarely made for the reasons indicated above, the temperature of ignition being only a few degrees (3 or 4) above the flash point.

**5. Degree of Refining.**—The extent of rectification of a light oil is indicated by the following tests:

(a) The oil is shaken with an equal volume of conc. sulphuric acid to ascertain if the latter appears coloured after separation.

(b) The oil is shaken with boiling water and the latter subsequently tested with litmus and with barium chloride.

(c) The liquid is boiled for a few minutes with alcohol containing a few drops of ammonia and then treated with silver nitrate to see if any brown coloration develops.

## **6. Detection and Determination of Benzoles.**

(1) DETECTION. (a) According to Holde, tar-pitch, previously washed with petroleum benzine (D 0.70–0.71) until the latter dissolves no more, is shaken with the light oil under examination. The latter becomes yellow or brown if tar benzoles are present.

Not less than 5–20% of benzoles are detectable in this way.

washed out with alcohol or the same solvent, the cylinder and the volume made up to 100 c.c. and the v  
Any nitro-derivatives formed from benzoles present pass int  
the alcohol, while the mineral oil remains undissolved; if th  
the latter has been diminished by 5 c.c., it is concluded that the  
benzoles.

This procedure is valid only for light oils composed of paraffin  
which are not attacked by nitric acid.

2. QUANTITATIVE DETERMINATION. This is effected by  
Böttcher's method, which is based on the absorption of aro  
carbons by sulphuric acid of D 1·84 at 15°, this being prep  
parts of conc. acid and 20 parts of fuming acid. In a flask h  
75 c.c., surmounted by a long neck graduated in 0·1 c.c. for 5  
of the oil are shaken for 15 minutes with 25 c.c. of the ab  
acid. After a rest of 30 minutes, concentrated sulphuric ac  
into the flask until the layer of benzine is entirely in the gra  
the volume of this being read off after the lapse of an hour. T  
between this volume and the original one represents the aro  
carbons.

7. Oil of Turpentine.—The procedure followed is that  
the detection of mineral oils in oil of turpentine (*see* Chapter o  
and its Products: Oil of Turpentine, 9, in Vol. II).

\* \* \*

*Crude light oils* are usually yellowish and often contain a cer  
of less volatile oils, but the *rectified* products should be colourle  
give negative results with the tests described under 5 (above).

*Rectified light oils* are subdivided, according to the temperat  
they distil, into different products, named differently in vari  
Usually the following products are distinguished:

Name.	Specific Gravity.
Light petroleum ether (Gasoline I) . . . . .	0·620–0·660
Heavy petroleum ether (Gasoline II, Light benzine) .	0·660–0·680
Benzine for pleasure automobiles } . . . . .	0·680–0·700
Benzine for ordinary automobiles } Petrols . . . . .	0·690–0·720
Benzine for heavy automobiles } . . . . .	0·720–0·770
Benzine properly so-called (Naphtha C) . . . . .	0·670–0·720
Ligroin (Naphtha B) . . . . .	0·707–0·730
Cleaning oil, Naphtha (Naphtha A) . . . . .	0·720–0·750
Substitute for oil of turpentine . . . . .	0·730–0·750

# LIGHTING OIL

Paraffin oil or kerosene, used for lighting purposes, is a clear mobile liquid, sometimes colourless, but usually more or less yellow and fluorescent and of characteristic odour. Physical as well as chemical tests are made.

## 1. Physical Tests

**1. Colour.**—The colour of lamp oil may be used as a basis for commercial contracts. Its intensity is determined by Stammer's colorimeter (Fig. 43), which consists of two vertical brass cylinders blackened inside, one of them, closed at the bottom by a glass, being charged with the liquid to be examined; in the other cylinder is inserted a standard glass coloured with uranium oxide to a definite intensity, and under both cylinders is a white reflecting surface. By means of two prisms, the two colours to be compared are observed in the two halves of the circular field of the eyepiece. The depth of the liquid may be varied by vertical displacement of the system of prisms along with a cylinder closed at the bottom by a glass disc and dipping into the cylinder of liquid. When uniformity of the field has been attained the depth of the liquid giving a colour intensity equal to that of the standard glass is read off on a scale.

The four grades of colour usually distinguished in the trade, with the corresponding depths in Stammer's colorimeter are :

Standard white.	.	.	.	50 mm.
Prime white	.	.	.	86.5 „
Superfine white	.	.	.	199 „
Water white	.	.	.	310 „ or more

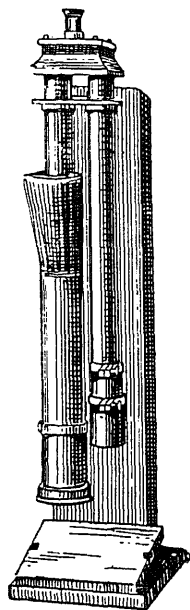


FIG. 43

In England and Russia, use is largely made of the Wilson colorimeter,<sup>1</sup> which contains four standard coloured glasses corresponding with the different commercial grades.

**2. Determination of the Specific Gravity.**—As with crude petroleum, at 15°.

For determining the density of lamp oil for fiscal purposes, the Italian Customs authorities use a thermo-aerometer graduated from 0.750-0.840, and tables of temperature corrections have been prepared.<sup>2</sup>



7. Its cover carries a thermometer *t* with a scale extending 50° and divided into half-degrees, and a clockwork mechanism motion by a lever *a*. Pressure of the latter opens automatic window in the cover and at the same time lowers a small flame

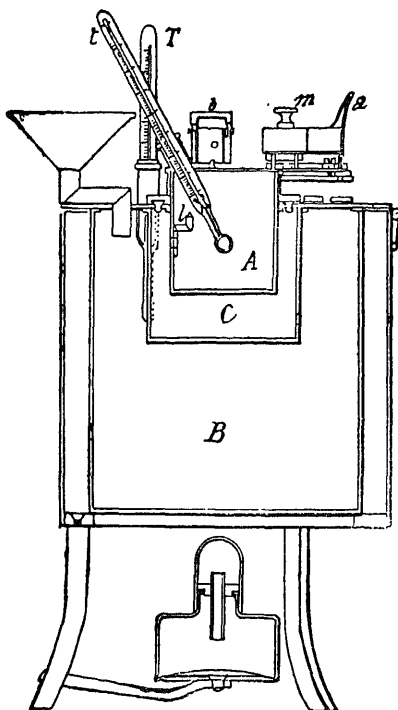


FIG. 44

aperture and then raises the window immediately. The entire movement should take two seconds.

The vessel *A* is heated in bath *B*, the intermediate space being left empty, and is on an ebonite ring fixed in bath *B*. The latter contains thermometer *T* with a red meniscus. The bath is first heated to a temperature, the cover containing the oil up to the level being fitted and thermometer *t* in the oil reads the rise of temperature of oil. The clockwork mechanism is operated and the test being repeated until a small explosion causes a small explosion. The temperature then shown is the point and should be corrected for the pressure ( $\pm 0.035^\circ$  below or above 760 mm) being returned to the normal degree.

The dimensions of all parts of the apparatus are exactly the same and with careful working the results should not vary by more than 0.1° at the most.

**5. Temperature of Ignition.**—When the flash point is measured, the cover of the vessel *A* is removed and a thermometer is reported in the oil, the heating being continued and, after each flame brought near the surface of the liquid without touching the oil fires, the temperature is observed, the thermometer is withdrawn and the oil extinguished with an asbestos card.

**6. Determination of the Viscosity.**—This is not usually done with illuminating oil, but it may, if required, be effected as in (q.v., Physical Tests, 7) or, more exactly, by means of the

**Determination of the Illuminating Power.**—This requires a *photometer*, one of those most largely used being that of Lummer and Brodigi (fig. 45), which is an improved form of the Bunsen type. It consists

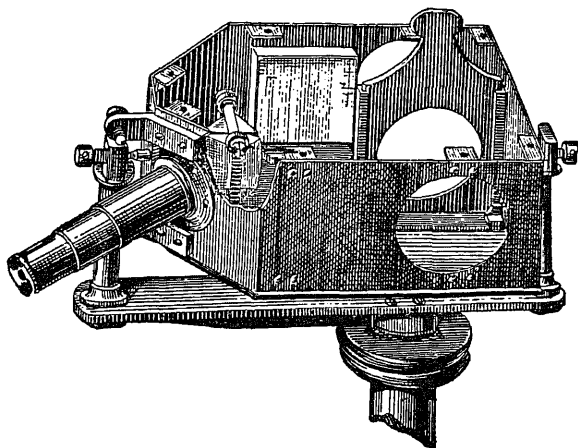


FIG. 45.

closed chamber with two opposite circular apertures, by means of which the two faces of a white screen in the chamber are illuminated respectively by the lamp to be examined and by a lamp chosen as unit. The two faces of the screen reflect the light, by means of a system of lenses, on to two concentric zones of the field of the telescope, as is shown to the left of the figure. When the screen is equally illuminated on both faces, the two zones of the field appear exactly similar. The two sources of light are placed at the extremities of a horizontal guide 3 metres in length and graduated in centimetres—the *photometric bench*. The position of the photometer is adjusted between the lights so that the field is uniformly illuminated: the intensities of the two lights are then proportional to the squares of their respective distances from the screen.

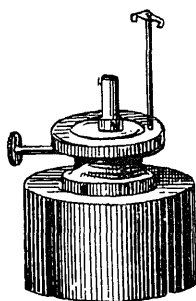


FIG. 46.

TABLE XLI

Unit.	Hefner Candle.	International Candle, Decimal Candle (Normal Candle), American Cand Pentane Candle.
Hefner candle . . . .	I	0.9
International candle, deci- mal candle (normal candle, American candle, pentane candle . . . . .	1.11	I
Carcel . . . . .	10.75	9.65

The petroleum to be tested is poured into a lamp and the lamp is centred on the photometric bench and lighted, the time being noted. The flame is kept low at first and is then gradually raised until it is as high as possible without smoking and without the wick charring excessively. Photometric observations are then begun and are repeated at regular intervals—the time of each being noted—until the oil is almost exhausted. The lamp is not being further moved; the lamp is finally extinguished and the consumption of oil being thus ascertained.

The position of the Hefner lamp is taken as the zero of the scale, that of the oil lamp as 300 cm.; the illuminating power of the lamp is then given by the formula,

$$i = \left( \frac{l - x}{x} \right)^2$$

where  $i$  is the intensity required, expressed in candles,  $l$  the length of the photometric bench and  $x$  the distance of the lamp from the screen from the zero point of the scale. The mean of the observations gives the mean intensity in candles.

The mean consumption per candle-hour is the quotient of the weight of oil used by the total candle-hours, and the yield of light (in candle-hours) produced per gram of oil is the amount of light (in candle-hours) produced per gram of oil divided by the total candle-hours by the weight of oil consumed.

It is necessary also to take account of the variation of intensity during the experiment. As a rule, after reaching a steady state a few minutes subsequent to the lighting of the lamp, it diminishes or less slowly to the end, mainly on account of the carbon

ption of oil being 180 grams.

Time.	Luminous intensity in candles.							
1st hour	.	.	.	.	.	.	.	9.50
2nd "	.	.	.	.	.	.	.	9.00
3rd "	.	.	.	.	.	.	.	8.50
4th "	.	.	.	.	.	.	.	8.00
5th "	.	.	.	.	.	.	.	7.50
Total candles								42.50

luminous intensity =  $42.50 : 5 = 8.50$  candles.

consumption per candle-hour =  $180 : 42.50 = 4.23$  grams.

l, or light produced per gram of oil =  $42.50 : 180 = 0.23$  candle-hour.

crease of luminous intensity =  $(9.50 - 7.50) : 9.50 = 0.21$ .

must be pointed out that petroleums of different quality do not burn well in all lamps, principally on account of the different quantities of require to burn completely. If the lamp does not allow access of t air the combustion, being incomplete, will give rise to smoke and ant smell, whereas excess of air in the flame will cool the latter too much inish the luminosity as well as the consumption. In general, Russian oils ore more air than the American, while with oils from the same locality, r is required by those rich in heavy and poor in light fractions. In any s necessary, to obtain comparable results, to work with the same lamps allow for the form and dimensions of their essential parts, namely, the burner and chimney. Marked influence on the course of the combus- also exercised by the wick, especially the length and quality of the fibre structure and compactness of the tissue; wicks of the same quality ensions should be used in all measurements, and they should be either washed thoroughly with petroleum ether and then dried.

**Behaviour at Low Temperature.**—This test is made on oils to in the open in cold places. A little of the oil is cooled for an hour, t-tube with a thermometer passing through its stopper, at the lowest ture to which it is likely the oil may be exposed, to ascertain if remains clear and mobile or if solid substances separate. For the re, *see* Heavy Oils, Physical Tests, 8.

## 2. Chemical Tests

**Acidity.**—This may be due to inorganic acids (principally sulphuric r to organic acids. The tests are made as follows:

**INORGANIC ACIDS.** The oil is shaken with tepid water containing methyl orange; if the colour changes to red, the aqueous layer is ed and tested with barium chloride.

If any appreciable coloration occurs, it is desirable to ascertain the rise of temperature takes place.

**3. Determination of the Sulphur.**—This is usually done with oils having a penetrating and unpleasant odour. The simple method that of Heussler and Engler,<sup>1</sup> this consisting in burning the oil in a suitable lamp, the chimney of which is joined to a bent tube containing 20 c.c. of 5% potassium hydroxide solution made just yellow and then left in the air to decolorise; the absorption vessel is connected with a pump. The lamp charged with the oil is weighed and the tube fitted and the suction adjusted so that the combustion is regular. The sulphurous anhydride produced is absorbed and then into sulphuric acid by the alkaline bromine solution. After a portion of the oil are burnt, the flame is extinguished, a little more air is drawn, the lamp again weighed and the sulphuric acid determined by gravimetric methods. The caustic potash used and also the air must, of course, be free from sulphur products.

The sulphur may also be determined by the Mahler calorimetric method (Crude Petroleum, Chemical Tests, 3).

#### **4. Distinction between Petroleums from Different Sources**

This is based mainly on the following tests:

(a) **SPECIFIC GRAVITY.** This is usually 0.780–0.805 for American and 0.820–0.825 for Russian lighting oils.

A better criterion than the specific gravity is furnished by the boiling points of the fractions obtained on distillation, these differing by about 10° in boiling points. Thus, the fractions of an American and a Russian petroleum distilling between 230° and 250° have the respective densities 0.809 and 0.820 and the fractions between 250° and 270° the densities 0.809 and 0.820.

(b) **TREATMENT WITH BROMINE.** 2 or 3 c.c. of American and Russian petroleum are not coloured when treated with a drop of bromine, but Russian petroleum becomes coloured under these conditions.

(c) **SOLUBILITY IN A MIXTURE OF CHLOROFORM AND ALCOHOL.** Halphen<sup>2</sup> has suggested a method based on the difference in solubility in a mixture of chloroform and aqueous alcohol, of fractions of different specific gravities from American and Russian petroleum. It is as follows: Several successive fractions of the oil are separated and the specific gravity of each of them determined at 15°C. A mixture in equal volumes of pure anhydrous chloroform and 95% alcohol necessary, when run in slowly from a burette with constant stirring to remove the turbidity produced, is then determined. The specific gravity of the fractions (which have about the same compositions with

and lamp oil should be clear and only slightly coloured (in time, however, it occurs if the oil is exposed to the air); its odour should be neither irritating nor unpleasant, as this would indicate the presence of sulphur compounds.<sup>1</sup> It should have no appreciable acidity and should not turn brown on exposure to phosphoric acid. For use in cold places, it should remain clear and mobile at a temperature lower than that to which it is likely to be exposed. The specific gravity is usually 0.780–0.805 for American and 0.820–0.825 for Russian

As regards *fractional distillation*, a good oil should not begin to distill at 100° and should contain only small amounts of light and heavy oils. The usually demanded for ordinary lamp oils are 5% of light oils and 10% of heavy oils, but the proportions actually present are well within these limits for good oils. As regards the fractions comprised between 150° and 300°, there should be no great disproportion between the amounts of these and the other fractions; the latter should predominate over the extreme.

The *flash point* is of importance as an indication of the danger attending the use of the oil. In Italy, legislation demands that the flash point for lamp oils determined by the Abel-Pensky apparatus, should not be below 21° C.

The *viscosity* of lamp oil, measured by the Engler apparatus at 20° C., is usually between 1.10–1.80, or, measured by the Ubbelohde apparatus, 1.10–1.80, and is usually lower for Russian than for American oils.

The *illuminating power* varies with the lamp used, but, under ordinary conditions, the consumption per candle-hour at 15–20° varies from 3.5 to 5 grams. The increase in luminosity from the beginning to the end of the combustion is usually greater with American than with Russian petroleum. The latter has a less initial and greater final luminosity than the former. In any case, with a good oil the decrease should not exceed one-fourth of the initial

Lamp oils from crude petroleum rich in solid paraffin, e.g., those from Pennsylvania, etc., if not properly prepared, deposit *solid paraffin* at 0°, but those of Russian origin remain clear even at – 20°.

The *calorific power* of lighting oil is 11,000–12,000 cal.

## MIDDLE OILS

### (Gas Oils)

These are intermediate in character to lighting oil and heavy oils. They are mobile and yellow to dark brownish-yellow, their density being between 0.845–0.855, their b.pt. 300–350°, and their viscosity below 3 (Engler). The most important determination with these oils is the yield of gas and the calorific value of the latter. The amount of gas given is determined in a small works plant. In the laboratory it may be ascertained approximately in comparison with a typical oil, in Ross and Leather's apparatus,<sup>2</sup>

According to Kissling and Engler (*Chem. Rev. Fett. Ind.*, 1906, p. 158), the pro-

consisting of a retort ( $23 \times 14.5 \times 12$  cm.) in which 15 c.c. is gasified. The temperature of gasification is measured with a thermometer and the volume of gas produced and the components absorbed in sulphuric acid determined.

Another apparatus for this purpose has been proposed and modified by Hempel.<sup>1</sup> The results obtained on the large scale are, however, not accurate, the best method being the work of Hempel.

The following determinations may also be required: Specific gravity, behaviour on distillation, flash point, viscosity, calorific power, etc., these being carried out as indicated in the articles dealing with *light* and *heavy oils*.

*Middle* or *gas oils* are used for making illuminating gas, for water gas, as a motive force, as a cleaning oil, and also as solvents.

The yields from 1 kilo of oil vary between the following limits: gas, 10–15 litres; tar, 300–400 grams; coke, 40–60 grams.

## HEAVY OILS

### (Lubricating Oils)

These oils vary somewhat in colour, appearance and consistency. The colour is usually reddish, brown or blackish, and marked with spots of rust also observed; some such oils are, however, colourless or nearly so, or not at all or but slightly fluorescent (vaseline oil). The specific gravity is to that of lamp oil if more volatile oils are present, but very low if not. The odourless. A bituminous smell indicates faulty refining and a resinous odour the presence of extraneous matter. As a rule they are liquid and more or less viscous, but some are highly molten and have almost the consistency of fats.

Analysis of lubricating oils aims at ascertaining if their properties are in correspondence with the uses for which they are designed under conditions fixed in the purchase contract.

Both physical and chemical tests are made.

### 1. Physical Tests

**1. Colour.**—This is usually compared with that of a standard oil by the means of the colorimeter (*see* Lighting Oil) or more simply by spreading equally thick layers of the two oils in similar rectangular

**Distillation.**—The flasks used for crude petroleum are employed. The temperature at which the distillation commences is noted and the residue is left up to 300–310°, representing the light oils and illuminating oil, and weighed.

For fiscal purposes (in Italy), the procedure followed is that indicated under *Petroleum*, 2. When decomposition occurs, recourse is had to distillation at reduced pressure, as indicated later for residues.

**Volatility.**—When heated, heavy oils begin to emit vapour at a certain point. To determine the quantities of the oil evaporating in a given time at different temperatures, in accordance with the conditions specified in contracts, the following procedure (Holde) is employed: A container *A* of the Pensky-Martens apparatus (Fig. 47) is charged to a certain mark with the oil and weighed. It is then heated for the prescribed time at temperatures between 100° and 200°, a glycerine bath is used, at higher temperatures (200–300°) a bath of a heavy cylinder oil having a flash point above 300° is employed.

The temperature of the oil is measured by means of a thermometer from the surface. The adhering oil is removed by a piece of filter-paper (previously washed with the crucible), which is added to the oil. After the experiment, the residue contained is cooled in water, dried, left in a desiccator for about 30 minutes and weighed; the loss in weight gives the volatile oil.

At temperatures higher than 300°, the oil may be heated directly in the Pensky-Martens apparatus.

**Flash Point.**—This is determined for heavy oils in the Pensky-Martens apparatus (Fig. 47). The upper view shows a section of the essential parts of the apparatus. *A* is a brass cylinder similar to that of the lower part of the apparatus and is fitted with a level gauge and a vaned stirrer *a*; it is placed inside an iron envelope *B* with very thick walls. This part of the apparatus is surrounded and protected from radiation by a cupola-shaped brass mantle and is heated by means of a triple burner *C*, a wire gauze being interposed. The cover of the vessel *A* carries a thermometer graduated from about 80° to 250°, with its bulb dipping into the oil and a gas flame *f* which is brought near to a small window and the cover is at the same time opened by turning a knob *b*. A fixed flame *l* serves as a check on the movable flame when this is extinguished by the explosion. The dimensions of the apparatus are fixed exactly.

The oil (previously dehydrated with calcium chloride if it contains water) is placed in the vessel *A* and the apparatus heated to 80°, after which the stirrer is started and the flame regulated so that the temperature rises about 5° per minute. Observations are made firstly at intervals of



ture rises about  $5^{\circ}$  per minute, a small flame being brought in contact with the crucible at regular intervals until a slight explosion occurs.

The results obtained by these two different methods vary in composition by  $5-40^{\circ}$ ; the method employed for the determination should always be indicated.

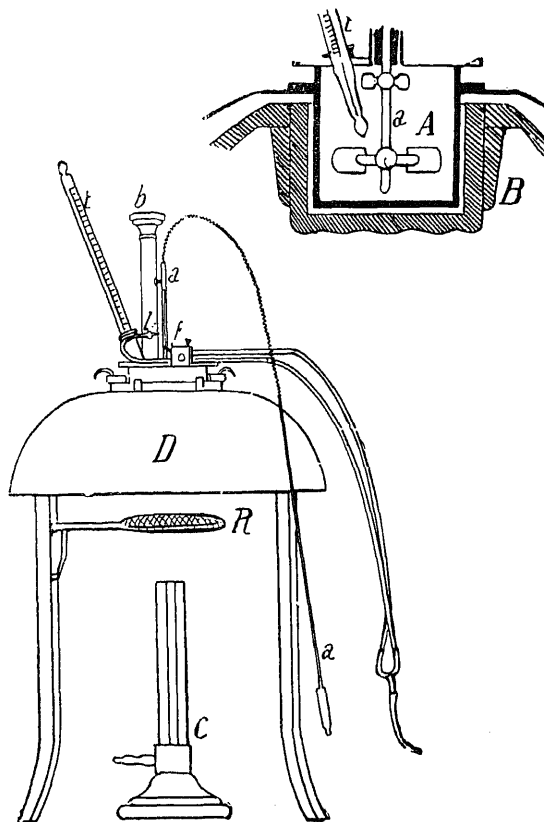


FIG. 47

**6. Temperature of Ignition.**—This determination may be considered the complement of that of the flash point—when an open crucible is heated—by continuing to heat so that the temperature rises from  $5^{\circ}$  per minute; a flame is held for 1-2 seconds near the surface of the crucible, the temperature of ignition being taken as that at which the sample ignites.

The temperature of ignition is usually  $20-60^{\circ}$  above the flash point.

temperatures  $c$  and  $d$  give the temperatures in the vessel  $A$  and in the bath, the latter is heated by means of a ring burner; the whole is supported on a tripod. Under the efflux tube is a glass flask  $C$  with marks on the stem at 200 c.c. and 240 c.c. All parts of the apparatus are of a standardised form and dimensions.

To make a determination, the central vessel is filled to the desired level with the oil to be examined and is dehydrated by decantation and passed through cotton wool dried at  $100^{\circ}$ , the efflux orifice being closed.

The outer vessel is then filled with water and heated carefully until the oil reaches the temperature at which the viscosity is to be determined. The flask is then placed beneath and the plug rapidly drawn, the time being counted from this instant. The time

taken to fill the flask to the 200 c.c. mark, divided by that taken under similar conditions, with a standard liquid, gives the viscosity of the oil in Engler degrees.

Usually a temperature of  $20^{\circ}$  is employed and water taken as the standard, the apparatus should be controlled from time to time with water; as 52–53 seconds are required for the efflux of 200 c.c. of water.

Between one determination and another of the time of efflux of water, the difference is  $\pm 1.5$  second, which corresponds with a difference of  $\pm 3\%$  in Engler degrees. If, then, the difference in the time of efflux of water is less than 1 sec., as prescribed for the use of the apparatus, the difference in the Engler is  $\pm 2.3\%$ .

Each apparatus is sold duly controlled, the time of efflux for water being stated.

For very dense heavy oils, and for such semi-solid products as vaseline, the viscosity should be determined at a higher temperature, e.g.,  $50^{\circ}$ ,  $60^{\circ}$ , or, sometimes,  $180^{\circ}$  or even higher. In the latter cases the whole apparatus is placed in a large oven, or use made of an apparatus in which the outer vessel—tightly closed and fitted with a reflux condenser—serves as a water-bath in which water ( $100^{\circ}$ ), aniline ( $180^{\circ}$ ) or other

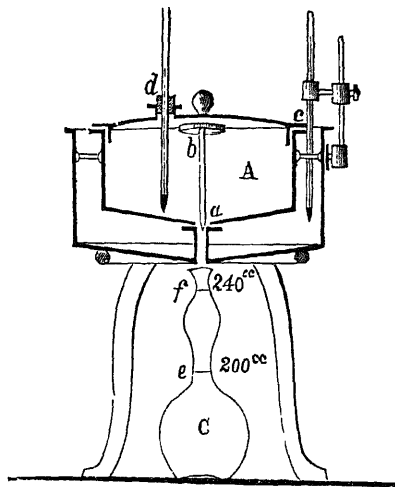


FIG. 48

machines, that of Martens<sup>1</sup> being most commonly employed

Viscometers of other types are those of Lamansky-Nobel<sup>2</sup> (Russia) and Saybolt<sup>4</sup> (America). In France us Barbey's *ixomètre*, which determines the coefficient of fluidity of an oil by measuring the volume of an oil dropping during a certain time.

The ratio between the values of the viscosity found by the Lamansky and Engler apparatus respectively is about constant and is 1.13 for light oils and 1.20-1.26 for more viscous oils (engine and cylinder oils), so that Engler degrees = number of Lamansky-Nobel degrees divided by 1.13.

The relations between Engler values and those obtained with the Redwood and Saybolt apparatus are given by the following formulae and  $t_e$  represent the times of efflux in the two apparatus and  $E$  the Engler value.

$$(1) \quad t_r = 192.2k \left( 1 + \sqrt{1 + \frac{0.01624}{k^2}} \right)$$

$$(2) \quad t_s = 228.7k \left( 1 + \sqrt{1 + \frac{0.01309}{k^2}} \right)$$

$$(3) \quad k = 0.08019E - \frac{0.07013}{E}$$

In practice, for viscosities which are not too low (not less than 10 Engler), it is a sufficiently close approximation to assume that the times of efflux in the Engler, Redwood and Saybolt forms of apparatus (under the conditions prescribed for each case) are in the ratios 100 : 100 : 100.

**8. Behaviour at Low Temperature.**—When strongly cooled, a lubricating oil first thickens and ultimately congeals and the aim of the test is to determine its behaviour is either to ascertain if the oil remains liquid at a certain temperature or to discover when it begins to thicken without becoming solid at a tallowy consistency.

In the former case a test-tube 15 mm. in diameter is filled with the oil to a height of about 3 cm. and placed, together with a thermometer, in a beaker about 12 cm. in height and diameter containing a saturated solution of a salt known freezing point<sup>5</sup> corresponding approximately with the temperature at which the oil should remain liquid. The whole is placed in a glass or earthenware vessel and cooled for an hour with a freezing mixture of equal parts of two parts of snow or pounded ice and one part of common salt. The mixture is then taken from the solution to see if the oil has remained liquid.

<sup>1</sup> D. Holde : *Untersuchung der Kohlenwasserstofföle und Fette*, Berlin, 1912.  
W. Hinrichsen : *Das Materialprüfungswesen*, Stuttgart, 1912.

<sup>2</sup> Wischinsin and Singer : *Chem. Rev. Fette Industrie*, 1897.

<sup>3</sup> B. Redwood : *Petroleum*, London, 1913.

<sup>4</sup> B. Redwood : *Petroleum*, London, 1913.

<sup>5</sup> For this purpose the following solutions may be used :

in a test-tube through the stopper of which passes a thermometer, and cooled in a freezing mixture; from time to time the tube is withdrawn for an instant and inclined, so that the temperature at which the oil begins to solidify may be discovered. A saline solution with a freezing point a little lower than this temperature is then chosen and the oil kept in the apparatus referred to above at the temperature found in the preliminary trial. At the end of the time the test-tube is removed from the solution and inclined so that an idea may be obtained of the degree of thickening; the latter may also be estimated by noting the adhesion of the oil to a glass rod when this is withdrawn.

Supercooling of the salt solution is avoided by scraping the congealed parts from the walls of the containing vessel or by withdrawing the vessel itself for an instant from the freezing mixture.

If the cooled oil is heated and another examination made of the behaviour at low temperatures, the result may be different from that of the first test; such difference may be due to the variations of temperature to which the oil is subjected during transport and storage. It is therefore useful to carry out the test on the oil, first as received and then after it has been heated to  $50^{\circ}$  for ten minutes and subsequently cooled for 30 minutes in a water-bath at  $20^{\circ}$ . With mixtures of mineral and fatty oils, the cooling should be protracted for 4-10 hours, one test being made without stirring the oil and the other with stirring every 15 minutes.

**9. Test of Fluidity at Low Temperatures.**—This is effected when required by pipetting the oil into a U-tube of definite diameter (usually 6 mm.), cooling the latter in a cooling mixture, and then measuring the change of level produced by applying at one side, for a definite period (generally 1 minute), a known pressure, e.g., 50 mm. of water, by means of a water manometer. The number of mm. measuring the change of level represents the degree of fluidity of the oil at the temperature of the experiment.

## 2. Chemical Tests

**1. Detection of Water and Solid Substances.**—These are usually recognised by the appearance and are investigated as with crude petroleum. Water may also be detected by heating the oil in a test-tube for about 15 minutes: if water is present froth is formed and drops of water appear in the cold part of the tube.

**2. Determination of the Acidity.**—Acidity is due either to mineral acids (sulphuric acid) introduced during refining or to organic acids.

(a) Acidity due to mineral acids may be detected by shaking 50-100 grams of the oil with double the quantity of distilled water, allowing the aqueous layer to separate, filtering it through a moist filter-paper and

c.c. of absolute alcohol and 50 c.c. of the separated alcoholic layer with decinormal alcoholic caustic soda in presence of phenolphthalein.

The acidity is expressed as sulphuric anhydride or oleic acid number of milligrams of potassium hydroxide necessary to neutralize 1 gram of the oil, the last being termed the *acidity number* of the oil.  $\text{SO}_3 = 7.05\%$  oleic acid = acidity number of 14.

**3. Alkalinity.**—This is detected by adding phenolphthalein to an aliquot part of the water with which the oil was shaken in the absence of the mineral acids; with free alkali a red coloration is observed.

It must be borne in mind that, if the oil in question contains any free alkali, the alkalinity found may be due to partial decomposition (hydrolysis) of the soap by water.

**4. Determination of the Solid Paraffin and Asphalt.**—A sample of petroleum (*q.v.*, Chemical Tests, 4 and 5).

**5. Detection of Oils, Fats and Waxes.**—(1) **QUALITATIVE.** 5 c.c. of the mineral oil are heated for about 15 minutes in a test-tube with a stick of caustic soda weighing about 4 grams, either over a naked flame or, better, in a paraffin bath at  $200-210^\circ$ . If fatty substances are present, even only to the extent of 1-2%, the whole mass becomes solid and brittle on cooling.

(2) **QUANTITATIVE.** If the qualitative test gives a positive result, a quantitative estimation may be carried out as follows:

(a) By the saponification number determined as indicated for the substances; about 5 grams of substance are used and, besides caustic potash, an equal quantity of benzene is added, the heating in a reflux apparatus being continued for about an hour. The saponification number obtained is divided by 1.85, the result being the percentage of fatty substances calculated from the mean value of their saponification numbers.

In presence of wool fat or waxes—which are usually detectable by their consistency and consistency—the results obtained are inaccurate, since these substances have saponification numbers different from those of fatty substances.

(b) By direct weighing, according to the directions given by Rodano<sup>2</sup>:

5 grams of the oil are saponified in a flask with alcoholic caustic potash solution (12 grams of caustic potash in 100 of alcohol), the flask being immersed in a bath of boiling water. As reflux apparatus, a simple retort is placed in the mouth of the flask, so that a large part of the

<sup>1</sup> According to H. Loebell (*Chem. Zeit.*, 1911, 35, p. 276), the acidity is determined by heating 10 c.c. of the oil with an alcohol-benzene mixture (2:1) as solvent and

which takes place fairly rapidly (in about half an hour).

Without evaporating off all the alcohol, the contents of the flask are poured into a separator and the flask thoroughly rinsed out, at first with small quantities of alcohol and then with ether. Sufficient water is added to dissolve the soap formed and sufficient ether to dissolve the mineral oil. The alkaline liquid is almost neutralised towards phenolphthalein by means of acetic acid and shaken, a sharp division occurring on standing between the ethereal layer containing the mineral oil and the soap solution. The ethereal liquid is separated, washed with distilled water until the alkaline reaction disappears, and distilled from a tared flask, the last traces of ether being expelled in a current of air.

The residue is dried in an air-oven at  $105^{\circ}$  for an hour and weighed ; the weight is multiplied by 20 and the product subtracted from 100, the remainder being the percentage by weight of the fatty substance.

To determine the nature of the fatty matter, the soap solution is treated with dilute sulphuric acid and the fatty acids collected and identified by their colour reactions and their physical characters (*see* chapter on Fatty Substances). If blown or oxidised oils have been added to the mineral oil, the fatty acids are brown, have an odour of vegetable oils and are soluble in ether, from which they are partially precipitated by petroleum ether ; the precipitated part has a pitchy appearance. In some of their characters, these fatty acids might be confused with those of fish oils, but the latter have a quite different odour and are precipitated by Halphen's bromine reagent (*see* Fish Oils), with which the fatty acids of oxidised oils give no precipitate.

When it is necessary to examine the characters of mineral oil changed by previous operations, the saponification is carried out in the cold as follows :

In a separating funnel, 50 grams of the oil, 200 c.c. of light petroleum ether and 200 c.c. of 10% alcoholic potash (in 95% alcohol) are vigorously and frequently shaken for about four hours and then allowed to settle, the ethereal layer being separated and washed several times by shaking with cold water, and the petroleum ether evaporated on a water-bath. The residue consists of the mineral oil ; its freedom from fatty matter may be ascertained by determining its saponification number, which should be almost zero.

**6. Detection of Alkaline and Alkaline-Earthy Soaps.—I. QUALITATIVE.** The alkaline soaps may be dissolved by shaking the oil with water, whilst the alkaline-earthy soaps are decomposed by shaking with hydrochloric acid : in this way the bases pass into solution in the hydro-

**7. Resin Oils.**—1. DETECTION. Resin oils are detected by their characteristic odour and by Morawski's reaction, which consists in treating a small amount of the oil in a test-tube with acetic anhydride and adding a drop of concentrated sulphuric acid (D 1.53): the appearance of a transient violet coloration in the presence of resin oil.

Resin oils may be detected also by shaking the oil (freed, if necessary, from saponifiable matter) with an equal volume of acetone and allowing the two liquids to separate, the acetone containing very little resin and almost the whole of the resin oil. If the solvent is evaporated, the resin oil in the residue may be characterised by the red coloration which it imparts to an equal volume of sulphuric acid (D 1.6), by its high specific gravity (0.970–0.980) and by its rotatory power.

2. DETERMINATION. Storch's method is used: 10 grams of oil (freed from saponifiable matters when these are present) are treated in a flask, at a gentle heat and with shaking, with 50 grams of 96% alcohol. After cooling, the alcoholic liquid is transferred to a weighed flask, the oily liquid washed with a little alcohol, which is also added to the flask. The alcohol is evaporated on the water-bath and the residue weighed. This residue is treated again with alcohol (10 times its weight), and the alcohol of the alcoholic solution giving a new residue (B). The mineral oil in this residue is calculated by means of the formula,  $\frac{(A - B)}{(a - b)}$ , where  $A$  and  $B$  are the weights of the two residues and  $a$  and  $b$  the quantities of alcohol used in their treatment. Subtraction of the calculated quantity of mineral oil from  $B$  gives the quantity of resin oil.

EXAMPLE: 10 grams of oil, treated with 50 grams of alcohol, gave a residue of 1.51 gram (A), and this, treated with 15.1 grams of alcohol, gave a residue of 1.15 gram (B). From the proportion

$$50-15.1 : 1.51-1.15 = 15.1 : x,$$

$x = 0.155$ . Amount of resin oil in 10 grams of the oil taken = 1.155 – 0.995 gram.

**8. Tar Oils.**—The presence of tar oils is recognised besides their characteristic odour, by the property they exhibit of reacting with nitric acid (D 1.45) giving nitro-derivatives, by their solubility in concentrated sulphuric acid on a water-bath with formation of compounds soluble in water, and by the general reactions of the phenols (*see Tar and Phenolic Acid*).

**9. Defluorescent and Odoriferous Substances.**—To detect the fluorescence of heavy oils,  $\alpha$ -nitronaphthalene is usually employed. The unpleasant fatty smell is masked by addition of a small

lene is converted into  $\alpha$ -naphthylamine, recognisable by its characteristic disgusting odour. The acid liquid is separated by means of a separating funnel, rendered alkaline with soda and extracted with ether, the ethereal solution being evaporated and the residue taken up in a little alcohol and treated with a drop of sodium nitrite solution acidified with acetic acid : the appearance of a yellow coloration changing to crimson indicates the presence of  $\alpha$ -naphthylamine.

\* \* \*

*Heavy mineral oils* have a specific gravity usually between 0.840 and 0.930, although occasionally the value 0.960 is attained. They should not contain any marked quantity of oils distilling below  $300^{\circ}$  and their flash point should not be below the specified limit laid down in relation to the purpose for which they are to be used. Usually this temperature is above, and often greatly above,  $140^{\circ}$ . Heavy oils are classified into numerous types having the following characters :

*Light oils for engines, gearing, motors and dynamos*, viscosity mostly 13-25 (at  $20^{\circ}$ ) and flash point  $180-220^{\circ}$ .

*Spindle oil*, very fluid, viscosity 3.5-15 (at  $20^{\circ}$ ), flash point  $160-200^{\circ}$ .

*Oils for compressors and refrigerating machines*, still more fluid than the preceding, viscosity 5-7 (at  $20^{\circ}$ ), flash point  $140-180^{\circ}$ ; the solidification point should be below  $-20^{\circ}$ .

*Automobile oils (cylinder)*, viscosity varying according to the season from 20 to 85 (at  $20^{\circ}$ ), flash point  $185-215^{\circ}$ .

*Pale heavy oils for engines and gearing*, viscosity 25-45 or more (at  $20^{\circ}$ ) flash point  $190-220^{\circ}$ .

*Dark heavy oils for locomotives and railway wagons*, viscosity 25-60 (at  $20^{\circ}$ ) and consistency varying with the season.

*Cylinder oils for steam engines*, boiling point high, very viscous ( $23-60$  at  $50^{\circ}$ ), moderately thick, flash point  $240-315^{\circ}$ , or, for some qualities,  $350^{\circ}$  or higher. These oils are divided further into low and high pressure cylinder oils.

Another type of heavy oil is that used for electric *transformers*. This should not contain water or mineral acids (reaction neutral) and should be non-volatile; when heated at  $100^{\circ}$  for some hours it should not decompose (in particular, it should not give solid products or become acid); it should retain sufficient fluidity at  $-15^{\circ}$  and should have a high flash point. The following requirements should be satisfied by such an oil : viscosity at  $20^{\circ}$ , 9.8 (Engler); specific gravity, 0.8825; flash point (Pensky),  $185^{\circ}$ ; volatility, determined by heating the oil for 5 hours at  $100^{\circ}$ , should not exceed 0.06%, or determined by heating for 2 hours at  $170^{\circ}$ , should not exceed 1%.

All the oils indicated above are subdivided into numerous types indicated by numbers or letters or are sold as special brands.

Oils to be used in the open air or in cold localities should not become turbid or solidify at a temperature somewhat below the minimum to which they may be exposed. As a rule American oils solidify at  $0^{\circ}$  or a little below, whilst those from Russia do not solidify above  $-10^{\circ}$  or  $-20^{\circ}$  or even lower.



as sulphuric acid). In dark oils, the acidity may reach 0.3% or, in some cases, 0.5%, but usually it does not exceed 0.15%. Mineral acids may be present.

## RESIDUES

The bituminous and pitchy residues from the distillation of heavy oils (mazut, astatki or ostatki) are blackish, only slightly transparent, of varying consistency, and of characteristic bituminous odour and composition products of difficultly volatile hydrocarbons.

The determinations and tests usually made are those of water, specific gravity, distillation, flash and ignition points, viscosity, and the amount of pitch and asphalt, the methods described for heavy oils being applicable. The calorific power and the sulphur are determined as in crude oils.

As regards *distillation*, these residues often decompose at high temperatures with formation of more volatile products, so that distillation methods already indicated may yield an amount of distillate less than the true value. This inconvenience is obviated by distilling the residue at reduced pressure (about 30 mm.)<sup>1</sup> from a half-litre flask with a side-tube connected with a sloping condenser, the lower end of which passes through a cork in the neck of a distilling flask similar to that used for the distillation of crude petroleum and having its side-tube in communication with an ordinary water pump. The distillation is continued until the thermometer marks 220°, the distillate being collected in a second flask; at the end of the operation, air is allowed into the condenser and the flask containing the distillate detached, the residue remaining in the first flask is distilled up to 300–310° at the ordinary pressure.

In determining the *flash point*, the residues often froth up at a temperature near 100° and overflow the vessel. In such cases the residue should be dehydrated as indicated for heavy oils. Extinction of the flame at 100° may be caused by residual traces of water in the product.

When the residues are to be used as fuel, the essential determinations are those of the calorific power and sulphur; the calorific value is expressed in calories.

## VASELINE

*Vaselines* of two sorts are sold: the *natural* ones, which consist of hydrocarbons semi-solid at the ordinary temperature, have colours varying from white to yellowish-brown, exhibit slight fluorescence and are somewhat sticky and ropy; and the *artificial* ones, which consist of

follows:

**1. Suspended Impurities.**—These are recognised by their appearance and are separated by fusing the product and filtering it in an oven.

**2. Mineral Matter.**—From 0.5 to 1 gram is burnt in a platinum dish to ascertain if any weighable residue remains. Any emission of odours of resin or of burnt fats during the combustion should be noted.

**3. Solubility in Alcohol.** **Reaction.**—One volume of the vaseline is shaken with two volumes of alcohol, the latter being separated and tested as to acidity or alkalinity and diluted with water to see if it becomes turbid.

**4. Behaviour towards Sulphuric Acid.**—10 grams of the melted vaseline are heated with 2.5 c.c. of a mixture of 5 parts of water with 15 parts of conc. sulphuric acid on a water-bath for 15 minutes, with frequent shaking, any browning of the acid or vaseline being noted.

**5. Detection of Fats.**—2 grams of the vaseline are boiled with a few c.c. of caustic soda solution, the cold aqueous layer being subsequently filtered off and acidified with hydrochloric acid: turbidity or separation of solid substance indicates the presence of fats.

**6. Detection of Resins.**—By Morawski's reaction (*see Heavy Oils, Chemical Tests, 7*).

**7. Viscosity.**—By means of Engler's viscometer (*see Heavy Oils, Physical Tests, 7*), working at 60° C. and keeping also the vessel into which the liquid flows hot.

**8. Determination of the Paraffin Wax.**—In a thin-walled, glass cylinder, 20 cm. tall and 3.5 cm. wide, a weighed quantity of about 0.5 gram of the vaseline is dissolved in the hot in 3 c.c. of ether, and the solution treated with 50 c.c. of 98% alcohol. After being cooled to 0° for an hour and filtered through a filter also kept at 0°, washing with a total quantity of 150 c.c. of 98% alcohol maintained at 0° (*see Figure, p. 338*), the insoluble residue is dissolved on the filter in hot benzene and the solution evaporated in a tared glass dish and the residue weighed. If the precipitate formed in the tube by addition of alcohol to the ethereal vaseline solution is not readily detached from the glass (as happens especially with natural vaselines and with those containing ceresine), the adherent part should be dissolved in benzene and this solution added to that previously obtained.

\* \*

*Pure vaseline* should melt to a clear liquid and should not contain mineral matter, or dissolve appreciably in cold alcohol, or exhibit an acid or alkaline reaction, or turn sulphuric acid brown. According to the Italian Pharmacopœia, pure vaseline for pharmaceutical use should be perfectly neutral and quite free from fats, and should leave no ash.

*Natural* vaselines have viscosities varying from 4.5 to 7.5 at 60° C. (referred to the temperature of 60° C. and determined with the Engler apparatus), whilst

*Crude paraffin wax* is coloured more or less intense yellow, whilst the *refined* product is a white or faintly yellow, translucent. The following tests are made:

**1. Suspended Impurities. Reaction. Behaviour to sulphuric Acid.**—As with vaseline (*q.v.*, 1, 3 and 4).

**2. Melting and Solidifying Points.**—The melting point is determined as with fats, use being made of a capillary tube blown into a bulb and with the lower end bent upwards after the substance has been introduced (*see Fatty Substances*, 4).

The solidifying point is determined with the Shukoff apparatus (*Fig. 49*),<sup>1</sup> consisting of a wide-mouthed bottle in which is fixed,

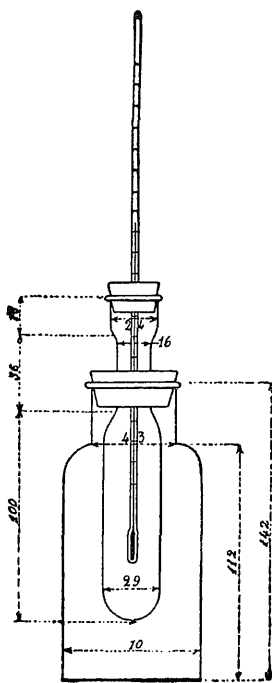


FIG. 49

a stopper, a tube of the dimensions shown. Through the stopper of the bottle passes a thermometer reading to the solidifying point.

In the inner tube 30–40 grams of the product are melted, and when the temperature of the fused mass is about 5° above the melting point, the apparatus is shaken and regularly until the contents become distinctly turbid and opaque. The shaking is then discontinued and the solidifying point observed.

The solidifying point is taken as the temperature at which the thermometer remains stationary during the cooling of the paraffin, or as the maximum temperature which it rises after a short arrest. When no large amount of stearic acid is present, only the temperature at which the mercury remains stationary is observed.

**3. Determination of the Paraffin** (in the crude product).—This is determined by Holde's method. From 0.5 to 1 g of substance is dissolved in the necessary

of ether, an equal volume of absolute alcohol being added and the mixture cooled to  $-20^{\circ}$ , the subsequent procedure being as described for petroleum (Chemical Tests, 4). The percentage found is increased to correct for the amount dissolved in the solvents.

With soft paraffin waxes this method gives less exact although satisfactory results.

about 200 c.c. of approximately 95% alcohol; the liquid is filtered, alcohol evaporated off and the residue examined. A yellow or brown indicates the probable presence of resin, recognisable by the reactions for heavy oils (Chemical Tests, 7); a white residue probably consists of stearic acid. In any case the nature of the residue may be ascertained by determining the acid and saponification numbers.

**Detection of Carnauba Wax.**—This is often added in small proportions to paraffin wax to raise its melting point. Indications of its presence are given by the characteristic aromatic odour and by the saponification number (zero for pure paraffin wax). When, therefore, the product has a saponification number, it is tested for carnauba wax, the following method being employed: 10 grams of the wax, chopped as finely as possible, are stirred for some hours with about 500 c.c. of ether, with frequent shaking. After filtration, the insoluble residue—in which the carnauba wax is concentrated—is washed with ether, pressed between absorbent paper and exposed to the air to dry. The saponification number is then determined and, if the presence of carnauba wax, is markedly higher than that of the original material. In doubtful cases the residue may be again treated with ether, and so on, to obtain a residue still richer in carnauba wax.

The melting point of the insoluble residue is also determined, this being usually considerably higher than that of the original material if carnauba wax is present. Finally, the carnauba wax may be identified by decomposing the residue obtained by means of an acid and determining the melting point of the separated fatty acids.

**Detection of Coal-tar Colours.**—Any colour in the paraffin wax indicates that a coal-tar colour may be present. To confirm this, the wax is extracted with alcohol and the solution tested as usual (*see* Coal-Tar Colours).

\*  
\* \* \*

*Good paraffin wax* should be white or only faintly yellow, neutral and free from suspended impurities, and should not render sulphuric acid appreciably turbid.

The melting point varies somewhat: ordinary hard paraffin waxes melt at 50–60°, whilst soft ones melt below 50° and in some cases at 30°. On the other hand, paraffin wax melting considerably above 60°, like that from kerosene occasionally found, but in general a product melting below 60° may be regarded as a paraffin wax, and one melting between 60° and 66° as a mixture of paraffin wax and ceresine (*see* later). Such limits are not valid if carnauba wax is present, 5% of this sufficing to raise the melting point by several degrees.

## CERESINE

with hot alcohol, allowing to cool, filtering, and evaporation of the filtrate on a slide. A crystalline appearance under the microscope indicates the considerable proportion of paraffin wax.

(b) DETECTION AND DETERMINATION BY THERMOTESTS (by *Armani* and *Rodano's* method) <sup>1</sup>: This is based on the different solubilities of paraffin wax and ceresine in a mixture of absolute alcohol and water in equal proportions.

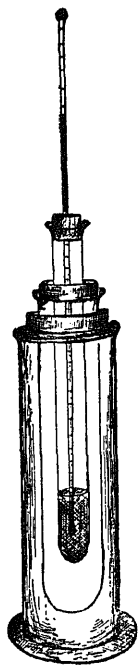


FIG. 50

Use is made of the apparatus represented in the illustration, consisting of a simple test-tube closed by a stopper and perforated to admit air and with a thermometer passing through it; the tube is surrounded by a larger one and by a glass cylinder on a foot. A mixture containing 0.1 gram of the product to be tested dissolved in the hot solvent, is placed in position and allowed to cool slowly, the temperature being noted at which precipitation of the dissolved substance takes place. In the case of paraffin wax by the appearance of either a turbidity or, with ceresine, a slight crystalline layer. A difference of 25° between the temperature of precipitation of paraffin wax (25°) and that of ceresine (50°) indicates the presence of even small proportions of paraffin wax.

by means of the following table :

Paraffin Wax. %	Ceresine %	Temperature of Precipitation.	Paraffin Wax. %	Ceresine. %
0	100	50°	70	30
10	90	48	75	25
20	80	47.5	80	20
30	70	47	90	10
40	60	44.5	95	5
50	50	43	100	—
60	40	41.5		

4. Detection of Resins and Fatty Acids.—See Paraffin Wax.

5. Detection of Carnauba Wax.—See Paraffin Wax.

6. Detection of Coal-tar Colours.—See Paraffin Wax.

7. Detection of added Mineral Matter.—This may be detected by the following tests:

a product with m.pt. above  $66^{\circ}$  is regarded as pure ceresine. Such a product, however, not valid if the ceresine contains carnauba wax.

## MONTAN WAX

### (Bergwachs)

*Montan wax* is obtained by the treatment of the lignites of Saxony. In appearance it resembles ozokerite or mineral wax, but in composition it is completely different.

*Pure montan wax* is black or dark brown, but the *purified* product is colorless or yellowish and of fibrous-crystalline appearance.

The determinations made are usually as follows:

**Melting Point.**—As for paraffin wax (*q.v.*, 2).

**Acidity.**—The product is dissolved at a gentle heat in a mixture of methyl and amyl alcohols (1 : 2) and the solution titrated with decinormal potassium hydroxide solution in presence of phenolphthalein (Holde's method).

**Saponification Number.**—About 2 grams of the wax are boiled 2 hours in a reflux apparatus with 40 c.c. of benzene and 25 c.c. of normal potassium hydroxide, the excess of the latter being subsequently neutralized with a seminormal acid.

**Unsaponifiable Substances.**—2 grams of the wax are saponified in benzene, the solution evaporated to dryness on a water-bath with 30 grams of anhydrous calcium chloride, and the residue extracted in a Soxhlet apparatus with petroleum ether.

*Pure montan wax* has m.pt.  $80-84^{\circ}$ , acid number 18-28, saponification number 80-90; the *purified* product has m.pt.  $83-84^{\circ}$ , acid number 93-100, saponification number 94-106.

## LUBRICANTS

Besides heavy mineral oils and vegetable and animal oils and fats (see preceding chapters), use is made as lubricants of mixtures of mineral oils with fatty oils (see Heavy Mineral Oils) and of complex mixtures which contain fats, resins, alkaline and alkaline-earthly soaps, mineral oils, and tar oils, in addition to water and mineral matter (lime, talc, etc.).

Among these complex lubricants the principal ones are the *stiff lubricants*, which include *cart-grease* and usually contain mineral or resin oils with soaps and mineral substances, and the *emulsive lubricants*, formed of

alcohol, water is present. The smell emitted when the substance on platinum foil gives an indication concerning the presence of oils, resins and fats. If ash is left, a little of the lubricant is dissolved in a mixture in equal proportions of petroleum benzine and absolute alcohol, the liquid being filtered after standing for some hours : the filtrate is investigated for lime and other extraneous mineral substances by the ordinary methods.

**2. Melting Point.**—This is determined empirically and as follows : The cylindrical bulb of a thermometer is covered with a thin layer of the lubricant, without heating, until the shining surface of the bulb is no longer discernible. The thermometer passes through the stopper of the test-tube about 18 mm. in diameter, the tube being immersed in a water-bath which is gradually heated. The temperature at which the lubricant begins to melt at the surface and that at which a drop of the liquid falls from the thermometer into the tube are noted.

**3. Water.**—On a boiling water-bath, 3-5 grams of the lubricant are heated in a tared glass dish with 10-15 c.c. of absolute alcohol, the liquid being stirred until no further frothing occurs and the liquid is clear. When cold, the weight is again taken, the loss representing the water.

The latter may also be determined by Marcusson's method (see page 100, *Leum*).

**4. Acidity.**—As a rule, stiff lubricants contain excess of alkali, but, however, they exhibit acidity, the latter may be determined by the method of Marcusson : 10 grams of the lubricant are heated in a retort with 50-100 c.c. of a neutral mixture of 90 parts of benzine and 10 parts of alcohol, any insoluble residue being filtered off in the hot and the filtrate mixed with the same mixture. The filtrate is mixed with 30 c.c. of 50% sodium hydroxide solution, the acidity measured by titration in the hot with normal solution of phenolphthalein.

**5. Detection and Determination of Soaps.**—From 10-20 grams of the lubricant are shaken vigorously and for a long time with 100 c.c. of dilute hydrochloric acid in a separating funnel, with 25 c.c. of dilute hydrochloric acid and 25 c.c. of ether ; on standing, two perfectly clear and well-separated layers should be formed. Both layers should be tested with litmus paper to see that they are distinctly acid ; if not, more hydrochloric acid is added and the liquid again shaken. The hydrochloric solution is then removed and tested in the ordinary way for bases, especially lime and soda, which occur in the soaps employed in lubricants.

The ethereal layer separated in the preceding operation is shaken with distilled water until neutral, and is then filtered and the filtrate is tested for bases.

a water-bath, the greater part of it being condensed. If any drops of water remain in the flask, they are eliminated by heating on a boiling water-bath after addition of a few c.c. of alcohol. The flask is again weighed when cold, the increase representing the fatty acids and resins present either free or combined as soaps, plus the neutral fats and non-saponifiable oils; the percentage of such substance may be denoted by  $a$ . The acid number is then determined on the whole ethereal extract in the flask itself; multiplication of the acid number by  $\frac{a}{200}$  gives the percentage ( $b$ ) of fatty (or resin)

acids found in the free state or as soaps. If from this is subtracted the amount of free acid—calculated with the same coefficient—found as under 4 (above), the remainder represents the acids of the soap; the amount of soap is then calculated in accordance with the nature of the base it contains.

**6. Detection and Determination of Neutral Animal and Vegetable Oils and Fats.**—The liquid remaining in the flask after the determination of the acidity is heated on the water-bath for about an hour with excess of alcoholic potash and the excess of the latter then titrated; this gives the saponification number of the neutral fats present. Multiplication of this number by  $\frac{a}{200}$  gives the percentage ( $c$ ) of neutral fat.

**7. Investigation of the Unsaponifiable Matter.**—The amount of this may be ascertained from the values already obtained (5 and 6), since it equals  $a - (b + c)$ .

When, however, it is necessary to separate and examine it, the procedure varies according as resins or resin soaps are present or absent.

In the latter case, about 50 grams of the lubricant are shaken vigorously with at least 200 c.c. of ether in a separating funnel until the oils are dissolved. A kind of emulsion holding the soaps in suspension is thus formed and filtration of this through a large pleated filter gives a clear ethereal solution containing, besides mineral oils, resin oils and tar oils, also any fats present. The ether is distilled off—the last traces being evaporated over a boiling water-bath—and the saponification number determined on a part of the residue. If there is any saponification number, fats are present; in such case, the non-saponifiable oils are separated by saponification in the cold (*see Heavy Oils, Chemical Tests, 5*), and the mineral, resin and tar oils investigated by the methods indicated for heavy mineral oils.

When, however, resins or resin soaps are present, to separate the non-saponifiable oils, the substance is extracted with acid ether (*see 5, above*), the ether evaporated, the residue washed with 90% alcohol to dissolve the resin, the insoluble residue saponified in the cold (*see Heavy Oils,*



8. **Detection and Determination of Free Lime and other Substances.**—About 10 grams of the lubricant are treated first in a reflux apparatus with 50 c.c. of benzine and 5 c.c. of alcohol, the residue being collected on a filter, washed with the benzine-alcohol, weighed and examined by the ordinary methods to see if it contains calcium carbonate, barium sulphate, talc, graphite and other substances.

\* \*

*Stiff lubricants* vary in composition according to the uses to which they are to be put. Those for stuffing-boxes in steam-engine cylinders are composed of a solid fat (tallow) or of a mixture of tallow with wax and oil. Ropes contain solid fats, wax, oil, talc, etc., and those for the chains and lifts, etc., are similar. Lubricants for rolling mills should melt at a low temperature; some are composed of pitch from fats or mixtures of this with creosote or pitch, while those with a basis of wool fat consist of partially saponified fat, with or without resin or acid resin oil. *Briquettes of vaseline* for rolling mills, are formed from mineral oil and soda soap.

Lubricants for gearing are composed of a stiff fat with graphite, oil, tar, resin, wax, paraffin wax and ceresine may also be added.

Lubricants for maintaining the flexibility of belting consist of a mixture with a solid fat (tallow, wool fat, wax). Adhesive lubricants for chains and pulleys contain, besides these fats, resin, resin oil, wool fat, etc.

Lubricants for the axles of vehicles usually contain tar oil in place of mineral oil and mixed lime and resin soaps in place of fatty acids.

## 2. Emulsive Lubricants

These are colourless, yellowish or reddish, and often fluorescent, and are mixed with water to form a kind of emulsion; they are sometimes sold ready emulsified and then have the appearance of milk. Besides observing the colour, transparency and odour, and determining the flash point, viscosity and behaviour at low temperatures, (see Oils, Physical Tests, 5, 7 and 8), the following tests are made (see also Turkey Red Oil, Chapter XI).

1. **Emulsivity.**—When shaken with water in any proportion it should give a milky emulsion, which should not separate on standing on a surface even after a long rest. When left overnight at the room temperature, the emulsion of 5 grams of oil with 100 grams of water should undergo no change or should at most deposit yellowish casein.

2. **Determination of the Water and of the Volatile Solvents.**—Emulsive oils may contain volatile solvents (alcohol, benzine, etc.) which are recognised by the smell or, better, by distilling the material over

a fixed residue remaining after calcining indicates the presence of fixed alkali.

(a) IN PRESENCE OF AMMONIA. The ammonia is determined by titrating the aqueous emulsion of the oil with N/2-hydrochloric acid in presence of methyl orange. From the amount of ammonia found, the quantity of fatty acids (regarded as oleic acid) combined with it is calculated (1 gram  $\text{NH}_3 = 16.542$  grams of  $\text{C}_{18}\text{H}_{34}\text{O}_2$ ). The total fatty acids are then determined by boiling the emulsion of the oil with a known quantity, in excess, of N/10-sodium hydroxide solution and titrating the excess of alkali with N/10-acid. The alkali used gives the total fatty acids (calculated as oleic acid) and this quantity, less the combined fatty acids, gives the free fatty acids.

(b) IN PRESENCE OF FIXED ALKALI. The free acids are determined by direct titration of the acidity in the usual way, and the total fatty acids by decomposing the soaps with hydrochloric acid, extracting the fatty acids with ether, washing the ethereal layer with water until free from hydrochloric acid, and titrating the acidity of this layer. The combined fatty acids are then given by difference. The aqueous layer is tested qualitatively for alkalies (*see also* Stiff Lubricants, 5).

(c) IN PRESENCE OF BOTH AMMONIA AND FIXED ALKALI. The ammonia, the fatty acids combined with it, and the free fatty acids are determined as in (a), the total fatty acids as in (b) and the fatty acids combined with the fixed alkali by difference.

**4. Detection of Unsaponifiable Substances.**—*See* Stiff Lubricants, 7.

## FATTY SUBSTANCES

Fatty substances consist essentially of combinations of the fatty series with glycerine, and are obtained from vegetables (especially seeds and fruits) and from various parts of animals. Those which are liquid at the ordinary temperature are termed *oils*, and those which are solid are termed *fats*.

The methods of analysis of fatty substances comprise the determination of certain physical and chemical properties, commonly known as constants, although they are constant only within certain limits, and also the results of investigations. The first part of the present chapter (*General Methods*) contains descriptions of the more important determinations and is worked out similarly on all fatty matters. The second part (*Special Methods*) is particularly with the more important fatty substances, the vegetable oils, fats, terrestrial animal fats and fats from fishes and other marine animals, being taken in order. For each class, tables are given showing the most important data relating to the characters of the fatty substances commonly sold.

Closely analogous to fatty substances are the *waxes*, which are esters of compounds of acids with higher alcohols rather than with glycerine. They will be treated after the fats, their general methods of analysis being the same.

The more important industrial products derived from fatty substances, such as stearine, oleine, glycerine, soaps, candles, etc., will be treated in the next chapter.

## GENERAL METHODS

## 1. Preparation of the Sample and Preliminary Determinations

Before analysis, a fatty substance must be freed from impurities or water it may contain. For this purpose, a portion of the sample is left for some time in an oven at about  $60^{\circ}$ , when it clarifies and melts completely if solid. It is then filtered through one or two layers of filter papers, care being taken that any water collected under the filter should fall on to the filter.

With some fats, especially industrial fats, the water, or other impurities (mucilaginous substances, residues of vegetable or mineral matter), and total fatty substances have to be determined.

A. DETERMINATION OF THE WATER. A flat-bottomed dish containing about 25 grams of coarse siliceous sand, previously ignited, and a glass rod, is dried at  $100-105^{\circ}$  and weighed. About 10 grams of the sample are then weighed exactly in the dish and mixed well with the sand. The dish is then heated in an oven at  $100-105^{\circ}$  and weighed at intervals of an hour until two successive weighings are not appreciably different. The loss in weight gives the water; the residue is utilised for determination C.

B. EXTRANEOUS (NON-FATTY) IMPURITIES. An exact weight (10-20 grams) of the substance is dissolved in a beaker in petroleum ether (b.pt. below  $70^{\circ}$ ) by heating gently on a water-bath. The solution is filtered through a filter dried at  $100-105^{\circ}$  and tared, the insoluble matter being washed on the filter with petroleum ether until a few drops of the filtrate leave no residue on evaporation. The filter and its contents are then re-dried at  $100-105^{\circ}$ , and reweighed, the increase giving the *non-fatty* matter.

This may also be deduced by subtracting water + total fat from 100.

C. TOTAL FATTY SUBSTANCE. The residue from A is placed in a filter-paper cartridge or capsule and extracted with ether or petroleum ether (b.pt. below  $70^{\circ}$ ) in an extraction apparatus. The ethereal solution is collected in a tared dish, evaporated on the water-bath and the residue dried at  $100^{\circ}$  and weighed.

To obtain the total fatty matter in the case of partially saponified fats (refinery residues and similar products) it is necessary to treat with ether, to shake with dilute sulphuric acid to decompose the soaps, to wash the ethereal liquid with water, to filter and evaporate it, and to dry the residue at  $100^{\circ}$  and weigh it. In this case the process indicated for turkey red oil (2) may also be followed (*see* next chapter).

If the respective quantities of free and saponified fats are required, the substance is first extracted alone with petroleum ether, the extraction being then repeated in presence of an acid.

## 2. Objective Characters

These characters are of importance in the analysis of fats, since, from the physical condition, colour and odour, at least an approximate idea of the nature of the substance may be obtained. Thus, the smell is sufficient to indicate whether a product is olive oil, tallow, palm oil, wool fat, etc.

## 3. Specific Gravity

This may be determined by means of a Westphal balance or picnometer at  $15^{\circ}$  with a liquid fat or at a higher temperature with a solid fat. In the latter case, determinations at  $100^{\circ}$  are especially convenient; the fat is placed in a wide test-tube immersed in a paraffin bath heated at  $100^{\circ}$ .

The most convenient and simple method for determining the solidifying point is as follows: Into a thin-walled glass tube blown to a small bulb in the middle (see Fig. 51) sufficient of the fused fat is sucked to fill about half of the bulb. When the fat has set, the branch *b* of the tube is bent into a U-shape in a small flame, and the tube then held in a water bath as long a time as possible (24 hours if convenient) and, if the

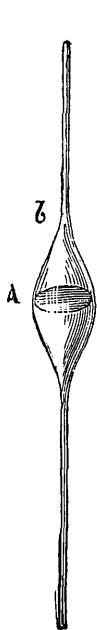


FIG. 51

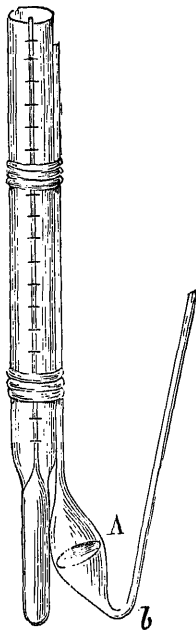


FIG. 52

a low temperature, in a cooling bath, the tube is then attached by means of a wire or a rubber ring to a thermometer (Fig. 52) so that the fat is in the upper part of the bulb, and the thermometer is suspended in a beaker of water which is slowly heated. At a certain temperature the fat begins to melt (at this temperature heating is discontinued) and the thermometer is held in the walls of the bulb to cool the lower part of the bulb. Note the temperature when the fat begins to melt and again when it is completely solid in the bottom of the bulb. These temperatures represent the *melting point* and *solidifying point* which the fat melts, i.e. the *solidifying point*.

The fat is then allowed to cool and note made of the temperature at which it begins to solidify again and when it is all solid, the *solidifying point* is determined.

The solidifying point may be determined more exactly by using a thermometer given for the solidifying point of fatty acids (see Tallow, p. 10). A similar method is used for measuring the melting points of fatty acids at the ordinary temperature and of those which become solid at high temperatures, but in such cases it is necessary to cool the mixture with water and ice, with ice alone, or with a freezing mixture of ice and salt.

These methods are also used for finding the melting and solidifying points of the free acids obtained from any fat by saponification (see below).

The melting and solidifying points, especially those of the

The object of this operation is the scission of fats into their components, i.e., into acids and glycerine (or, with waxes, higher alcohols). It is effected as follows: In a conical flask or a porcelain dish, 20 grams of the fat are heated on the water-bath, with frequent stirring, with 15 c.c. of 50% aqueous caustic potash solution and 30–40 c.c. of 95% alcohol until the liquid becomes homogeneous and clear, this usually occurring after about half an hour.

With substances either containing higher alcohols (wool fat, waxes) or mixed with unsaponifiable substances (mineral oils, various extraneous matters), a clear liquid is not, however, obtained, since the action of the potash causes the separation of the higher alcohols, hydrocarbons and other unsaponifiable substances, which are usually insoluble under the conditions employed. In such a case it is well in order to ensure complete saponification to prolong the heating for an hour or more, with frequent shaking. In some instances, for example, with wool fat or waxes, it is necessary to carry out the reaction under a certain pressure. For this purpose, use is made of a round-bottomed flask, closed with a stopper carrying either a two-bulbed safety funnel charged with mercury or a right-angled tube dipping 5–6 cm. below the surface of mercury in a beaker. In other cases, for special investigations on non-saponifiable substances, *saponification in the cold* is employed; this is effected by dissolving the substance in ether or petroleum ether, adding a considerable excess of alcoholic caustic potash solution and shaking for a long time.

When the saponification is finished, the product (soap) may be used for various purposes, such as the examination of the unsaponifiable substances or higher alcohols (*see* 19: Unsaponifiable Substances), the determination of the glycerine (*see* Glycerine), or the separation of the fatty acids.

For the last purpose, the product of the saponification is first freed from alcohol by prolonged heating on a water-bath, the residue being dissolved in hot water, the hot aqueous solution shaken well with excess of dilute sulphuric acid and left at rest on the water-bath until the fatty acids are collected at the surface of the aqueous liquid in a clear layer. The water above the fatty acids is then siphoned off and replaced by fresh hot water, with which the acids are stirred, this washing being repeated three or four times. Instead of siphoning off the water, the latter and the fatty acids may be decanted on to a moist filter and the acids washed with hot water on the filter itself until the filtrate ceases to give the reaction for sulphuric acid. The washed fatty acids, in a flat dish, are kept for some time (about an hour) in a steam-oven and then filtered through a dry filter. They are then ready for various determinations, such as the melting and solidifying points, acid number, iodine number, solid and liquid acids.

The test of solubility in the ordinary solvents, e.g., in ether, if a fatty substance is pure or mixed with extraneous substance that solvent. The test of solubility in alcohol may be used to distinguish oil and fatty acids in general (easily soluble even in the cold) from other oils and fats, which are mostly very slightly soluble, especially in cold.

## 7. Acid Number (Acidity Index)

The acid number is defined as the number of milligrams of potassium hydroxide (KOH) necessary to neutralise the free fatty acid in the fatty substance. From this number the amount of free acid in a fat may hence be deduced. The determination is made as follows:

An exact weight of about 5 grams of the fat is heated in a flask on a water-bath with 50–60 c.c. of 96% alcohol,<sup>1</sup> and kept until the alcohol begins to boil. Seven or eight drops of phenolphthalein solution (1% in 95% alcohol) are then added and the liquid is titrated with decinormal potassium hydroxide solution until a persistent pink coloration appears. If solid fat separates during the titration, the flask is removed from the water-bath until the fat melts. The volume of potassium hydroxide solution gives the acid number (1 c.c. N/10-KOH = 0.00561 gram of KOH).

From the acid number thus obtained the percentage of free fatty acid in a fat may be calculated; this is usually expressed as oleic acid, the molecular weight of which is 282 (corresponding with 56.1 of KOH). The calculation is made by the formula,

$$x = \frac{n \times 0.0282}{p} \times 100,$$

where  $n$  is the number of c.c. of N/10-KOH used,  $p$  the weight of the substance and  $x$  the percentage of oleic acid in the substance.

The free acids in a fat are sometimes expressed as sulphuric acid ( $\text{SO}_3$ ), the formula then becoming

$$x = \frac{n \times 0.004}{p} \times 100,$$

$x$  in this case being the percentage of  $\text{SO}_3$ .

EXAMPLE: For 5.223 grams of fat, 4.2 c.c. of N/10-KOH were used. Since 1 c.c. of the potash corresponds with 0.00561 gram of KOH, the acid number will be

$$\frac{5.61 \times 4.2}{5.223} = 4.51.$$

$$\text{Percentage of oleic acid} = \frac{4.2 \times 0.0282}{5.223} \times 100 = 2.267.$$

$$\text{Percentage of SO}_3 = \frac{4.2 \times 0.004}{5.223} \times 100 = 0.321.$$

The acidity of a fat may also be expressed in *degrees*, which are distinguished as *Köttstorfer* and *Burnstyn* degrees. The former represent the number of c.c. of normal KOH solution necessary to neutralise the free acidity of 100 grams of a fat.

Burnstyn degrees (formerly used, especially to express the acidity of lubricating oils) represent the number of c.c. of normal KOH required to neutralise the acidity of 100 c.c. of oil, the test being carried out as follows : 100 c.c. of the oil are shaken with 100 c.c. of 90% alcohol ; when the latter has separated and become clear, 25 c.c. of it are titrated with normal KOH, tincture of turmeric or phenolphthalein being used as indicator. The number of c.c. used, multiplied by 4, gives the Burnstyn acidity of the oil.<sup>1</sup>

Interconversion of the acidities expressed in different ways may be effected by means of the following table :

Acid Number (mgrms. KOH per gram of substance).	Oleic Acid. %	Sulphuric Anhydride. %	Köttstorfer Degrees (c.c. N-KOH per 100 grams of substance).
1	0.5027	0.0713	1.782
1.9893	1	0.1418	3.546
14.0250	7.0500	1	25.000
0.5610	0.2820	0.0400	1

The acid number of fatty substances is very variable. As a rule, fresh or recently-prepared fats contain little or no free acid. With keeping, especially if not well protected against the simultaneous action of air and light, the acidity increases, slowly at first and more rapidly later. The acid number is of importance in judging edible oils and lubricants, neither of which should contain more than certain limiting proportions of free acid.

## 8. Saponification Number

By saponification number is meant the number of milligrams of potassium hydroxide (KOH) necessary to saponify completely 1 gram of a fatty substance. From this number the quantity of total acids, either free or combined, in a fat may be deduced. The determination is made as follows. :

REAGENTS required are :

(1) *Alcoholic caustic potash solution* (about seminormal). Prepared

1. dissolving about 20 grams of pure caustic potash in a little water and



being emptied in the same way. The flask is closed through which passes a glass tube about a metre long to serve as a condenser and heated on a boiling water-bath, with occasional shaking for half an hour or rather more (*see* Saponification, 5).

The flask is then removed from the bath and the excess of alkali is being free titrated with seminormal hydrochloric acid in presence of 2 drops of the phenolphthalein solution.<sup>1</sup>

A *check* experiment with 25 c.c. of the caustic potassium (without fat) is made at the same time and under the same conditions as the actual test.<sup>2</sup>

From the difference between the volumes of seminormal hydrochloric acid used in the check experiment and in the actual test the amount of potassium (milligrams) necessary for the complete saponification of 1 gram of the fat is calculated.

**EXAMPLE :** 1.524 gram of a fat, saponified with 25 c.c. of a seminormal potassium hydroxide solution required 11.9 c.c. of seminormal hydrochloric acid to neutralise the excess of potassium hydroxide. In the check experiment, 22.5 c.c. of the acid were required to neutralise 25 c.c. of alcoholic potassium hydroxide. Since 1 c.c. N/2-HCl = 0.02805 gram of KOH, the amount of KOH necessary to saponify 1.524 gram of fat is (22.5 - 11.9) c.c. = 10.6 c.c. = 0.2973 gram, so that the amount for 1 gram of fat is 0.195. The saponification number of the fat is hence 195.

The saponification number is of importance for distinguishing between different fats and waxes and especially for the analysis of mixtures of fatty substances with non-saponifiable matter (mineral oils, resin oils, etc.).

The majority of fatty substances have a saponification number between 180 and 200, but the oils of the Cruciferae (colza oil, rapeseed oil, etc.), the oil of grape-seed, and a few other oils, have values below 190.

Coconut oil, palm-kernel oil, certain other vegetable fats, and waxes have saponification numbers above 200. Waxes have very low saponification numbers.

## 9. Ester Number

The ester number denotes the number of milligrams of potassium hydroxide necessary to saponify the neutral fat (neutral esters) in one gram of the substance. With fats which do not contain free acids, the ester number is equal to the saponification number ; when, however, free acids are present, the ester number is less than the saponification number.

To determine the ester number, a little powdered calcium carbonate is added to the fat at such a rate that 50 c.c. of the liquid pass over the calcium carbonate. To test the distilled alcohol, 10 c.c. are boiled with 1 c.c. of 50 % caustic potassium hydroxide solution and the liquid allowed to stand for 20 minutes to see if any colour is developed. If the alcohol is unsuitable for preparing alcoholic potassium hydroxide solution, it should be replaced with permanganate.

<sup>1</sup> When the fat gives a highly coloured solution with the alcoholic potassium hydroxide solution, it is advisable to dilute the liquid considerably with neutral alcohol before titrating. The neutral point may be determined with accuracy.

the ester number is given by the difference between the acid and saponification numbers.

The ester number has importance especially for the analysis of beeswax.

### 10. Volatile Acid Number (Reichert-Meissl Number)

By this is meant the number of c.c. of decinormal alkali necessary to neutralise the volatile acids, soluble in water, obtained from 5 grams of a fatty substance under definite conditions.

Reichert's original method has been modified in various ways, the modification proposed by Leffmann and Beam and by Polenske being now preferred.

In a flat-bottomed, 300 c.c. flask of resistant glass (A), exactly 5 grams of the fatty substance (filtered oil or molten fat) are heated over a small flame with 20 grams of pure glycerine and 2 c.c. of caustic soda solution (100 grams of pure sodium hydroxide in 100 grams of water) until the liquid froths and becomes clear and homogeneous (5-8 minutes). The liquid soap thus obtained is allowed to cool to 80-90° and is then shaken with 90 c.c. of distilled water at the same temperature, and heated if necessary, until solution is complete. 50 c.c. of dilute sulphuric acid (25 c.c. of the pure conc. acid to the litre) and 0.6-0.7 gram of roughly powdered pumice are then added and the liquid distilled into a 110 c.c. flask.

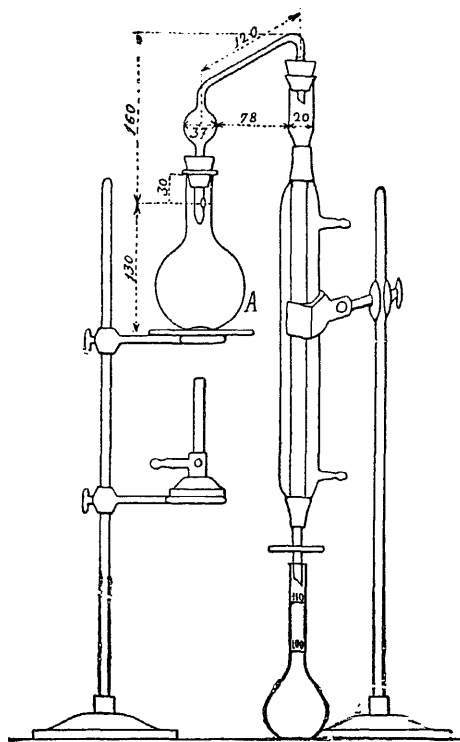


FIG. 53

required, increased by one-tenth, represents the volatile acid number.

For each series of determinations a blank experiment is run with the same glycerine (20 grams), sodium hydroxide solution and sulphuric acid (50 c.c.) and under the same conditions as the test. The number of c.c. of N/10-alkali used in this blank test is subtracted from the volume used in the actual test.

The determination of the volatile acid number may be carried out with that of the Polenske number (*see* Butter, 15, in Chapter 10).

The Italian official method for determining the volatile acid number for oils, Wollny's modification of the Reichert-Meissl method, and the Leffmann and Beam's modification, which differs from that described in using a glycerine and soda solution previously prepared (125 c.c. of 5% sodium hydroxide solution heated until the water has evaporated) in place of glycerine and soda separately, and in a few other particulars.

The volatile acid number is of importance in the analysis of fats, principally butter. With most oils and fats, the number is less than 1; coconut oil, palm-kernel oil, croton oil, cacao butter and other fats have numbers above 1 (up to 14), while for butter the number is usually between 1 and 2. Some fish oils and other marine animal oils (dolphin, whale) have sometimes moderately high volatile acid numbers.

## 11. Acetyl Number

This represents the number of milligrams of potassium hydroxide corresponding with the quantity of acetyl ( $C_2H_3O$ ) combining with 1 gram of fat or wax, or, more usually, with 1 gram of fatty acids or hydrolyzable (unsaponifiable substances) obtained from a fat or wax.

This number is determined as follows: About 20 grams of the fat or of the free fatty acids obtained in the manner described under "Saponification" (*see* 5, above) or of unsaponifiable substances (highly purified) obtained as indicated under "Non-saponifiable Substances" (Chapter 10) are boiled for 2 hours with an equal volume of acetic anhydride in a flask fitted with a reflux condenser, the mixture being subsequently poured into a beaker, mixed with 500 c.c. of hot water and boiled for 10 minutes. The supernatant water is then siphoned off and the residue washed in the same way, this treatment being continued until the water washes become acid; this usually requires four or five washings. The product is then filtered through a dry paper in an oven at 100°C. for the determination of the acidity number—known as the *acetyl acidity number*—and the saponification number—the *acetyl saponification number*. The acetyl number is given by the difference between these two numbers.

For these determinations, 3-5 grams of the acetylated

KOH, the acetyl acid value being therefore

$$\frac{485.2}{3.402} = 142.6.$$

After addition of a further quantity of 30 c.c. of N/2-KOH and boiling, 11.5 c.c. of N/2-HCl were necessary to neutralise the excess of potash. The potash consumed in the saponification of the acetyl compounds was hence  $30 - 11.5 = 18.5$  c.c., corresponding with  $18.5 \times 0.02805 = 0.5189$  gram KOH; for 1 gram of acetylated acids the amount of KOH will be

$$\frac{518.9}{3.402} = 152.5.$$

The acetyl number is therefore 152.5, and the acetyl saponification number,  $142.6 + 152.5 = 295.1$ .

The acetyl number is related to the quantities of hydroxylated acids and higher alcohols in the fatty substances, these being especially large in castor oil, grapeseed oil, waxes and blown or oxidised oils. It is consequently of some importance for the identification of these fats and for the analysis of waxes.

## 12. Iodine Number

This expresses the number of grams of iodine 100 grams of a fatty substance are capable of fixing under definite conditions. It may be determined in the two following ways:

**A. Hübl's Method.**—REAGENTS required:—

1. *Iodine solution.* 25 grams of iodine are dissolved in 500 c.c. of 95% alcohol (puriss.); in another 500 c.c. of the same alcohol, 30 grams of mercuric chloride are dissolved and the solution filtered, if necessary. The two solutions are stored separately in tightly stoppered bottles in a cold dark place, equal volumes of them being mixed in the quantities required for the number of tests to be made, about 48 hours before use.

2. *Potassium iodide solution.* 10 grams of potassium iodide (puriss.) quite free from iodate are dissolved in 100 c.c. of water.

3. *Starch solution.* 1 gram of starch is made into a paste with a little cold water and then poured into about 300 c.c. of boiling water, stirred and left to settle; when cold, the clear supernatant liquid is poured off for use as indicator. *Soluble starch* also may be employed, this being prepared by digesting potato starch with dilute hydrochloric acid (D 1.05) for a week, then washing with water by decantation until the washing water is free from hydrochloric acid and drying between filter-papers at a moderate temperature; 1 gram of this starch is dissolved in 100 c.c. of hot water.

4. *Sodium thiosulphate solution.* 25 grams of crystallised sodium thiosulphate (puriss.) are dissolved in distilled water to 1 litre, and the strength of the solution determined by Volhard's method, as follows: 20 c.c. of a solution containing 3.863 grams of pure potassium dichro-

acid, the number of c.c. of thiosulphate used corresponds of iodine.

5. *Chloroform*, which should be pure.

PROCEDURE. In a thin glass bulb the fatty substance (as or fused if a solid, but always previously dehydrated and for Preparation of the Sample) is weighed, 0.1–0.2 gram being taken for a drying oil, 0.2–0.3 gram of a semi-drying oil, 0.3–0.4 gram of a non-drying oil, 0.4–0.8 gram of a solid fat. The bulb is placed in a half-litre bottle with a tight ground stopper, the bottle being held obliquely and shaken so as to break the bulb against the walls. The fat is dissolved in 15 c.c. of chloroform and treated with 25 c.c. of the mercuric iodide solution (prepared 24 hours earlier), care being taken in all cases to empty the pipette the same way so that exactly the same volume of solution is used. The bottle is carefully shaken and the bottle stoppered and kept in a dark place at (15–18°) for 4–6 hours with non-drying or semi-drying oils, 1–2 hours with drying oils. At the end of this time, 15–20 c.c. of the sodium iodide solution are introduced, the stopper, neck and walls of the bottle being washed with this solution and with about 200 c.c. of water, which is subsequently added. The excess of iodine is then titrated with the sodium sulphate solution, which is slowly run in until the aqueous layer and the chloroform beneath appear only pale yellow; about 5 c.c. of the sodium sulphate solution are then added and the titration completed.

This test is always made in duplicate and at the same time. The control experiments are carried out with the same proportions of reagents, but under the same conditions, but without the fatty substance. The amount of iodine in the two checks are titrated one before and one after the actual test, the mean value being taken.

This mean is deducted from the mean value obtained in the test of the fat, the remainder representing the amount of iodine actually combined with the fat, and this, calculated as percentage, is the iodine number.

**B. Wijs's Method.**—In this method, the alcoholic solution of iodine and mercuric chloride is replaced by an *acetic acid solution of iodine and mercuric chloride* prepared as follows:

8 grams of pure iodine trichloride and 8.5 grams of mercuric chloride are dissolved separately in pure glacial acetic acid (99%) on a water bath, in dry, closed vessels to avoid absorption of moisture. When the solutions are transferred to the same 1-litre flask and made up to 100 c.c. with pure glacial acetic acid.

It is necessary to ascertain that the acetic acid is at least 99% pure.

of contact of the fatty substance with the iodine solution is reduced about an hour for non-drying or but slightly drying oils and fats and to about two hours for the others. The calculation is made as with Hübl's method.

EXAMPLE: For 0.352 gram of olive oil 24.90 c.c. of thiosulphate were used, and in the check experiment, 48.80 c.c. The quantity necessary to oxidise the excess of iodine is, therefore,  $48.8 - 24.9 = 23.90$  c.c. Assuming that 0.2 gram of iodine corresponds with 16.5 c.c. of thiosulphate, 0.01212 gram with 1 c.c., the amount of iodine absorbed by 0.352 gram of oil is  $23.9 \times 0.01212 = 0.2896$  gram, so that the iodine number is

$$\frac{0.2896 \times 100}{0.325} = 82.27.$$

As a rule the iodine numbers obtained by the second method (Wijs's) are higher than those given by Hübl's method.

The determination of the iodine number is of great importance for the analysis of fatty substances, since it serves to characterise many of them and to indicate whether they are pure or mixed. Drying oils (linseed, hempseed, walnut, poppy-seed, madia, Japan wood, etc.) and fish oils (sardine, anchovy, herring, cod) have very high iodine numbers, which usually exceed 120. The non-drying oils (olive, arachis, almond) have iodine numbers below 100. The semi-drying oils (colza, cottonseed, sesamé, maize) have intermediate values. Iodine numbers between 30 and 60 are usually shown by vegetable fats, excepting coconut oil and palm-kernel oil and certain so-called vegetable waxes (myrtle, Japan), which have values below 11. With the animal fats the iodine number is not high, being usually less than 90.

With each individual fat the iodine number may vary between fairly wide limits, in accordance with the method of preparing the fat, with the degree of maturity of the fruit or seed yielding it, with the conditions of storing and of the fat, etc. Very wide variations are, however, exceptional, and in some cases the iodine number keeps moderately constant (*see*, for example, *Oil*), so that it may be used for the approximate determination of the relative quantities of fats in a mixture of two of known character—the calculation being made according to the law of mixtures.

The causes of pronounced variations in the iodine number are various, but of special importance are the age and storage conditions of the fat. In general, old and badly stored (rancid) fats have iodine numbers lower than those of corresponding fresh and well-kept fats; this is notably the case with drying oils which readily absorb atmospheric oxygen.

### 13. Absolute or "Inner" Iodine Number

This represents the weight of iodine absorbable by 100 parts of the liquid fatty acids obtainable from a fatty substance.<sup>1</sup> It is determined by the liquid fatty acids isolated by Tortelli and Ruggeri's process (*see* later :

and lower in the non-drying oils (about 100). For animal fats usually 90-100, but in rare cases slightly exceeds 100 (in some). This number is of especial importance in the analysis of lard and tallow (see Lard).

## 14. Insoluble, Fixed Fatty Acid Number (Hehner Number)

This number represents the quantity of non-volatile fatty acids in water contained in 100 grams of a fatty substance. The determination is carried out as follows:

5 grams of the fat, weighed into a conical flask, are mixed with 5 c.c. of 90% alcohol and 5 c.c. of 50% caustic potash solution. The flask is closed with a stopper through which passes a long glass tube, a reflux condenser and is then heated on a water-bath with stirring until saponification is complete. The stopper and tube are removed and the alcohol distilled off, the last traces being expelled by heating the flask in a boiling water-bath. The soap is dissolved in 150 c.c. of water and then decomposed with a slight excess of dilute sulphuric acid. The flask is then left on the water-bath until the fatty acids have formed a homogeneous layer at the surface, after which it is allowed to cool somewhat and kept in cold water (at 10-15°) for about an hour, until the acids set to a solid mass. The aqueous liquid is then filtered through a smooth, thick paper filter, previously dried at 100° and weighed in a bottle. A further quantity of 200 c.c. of hot water is added to the residue which is shaken, left on the water-bath for 15 minutes, filtered, washed somewhat and placed in cold water, the aqueous liquid being removed as before. This treatment is repeated five or six times until the residue no longer reddens a litmus paper immersed in it for 10 minutes. The fatty acids are then completely melted by addition of a little benzene and the whole transferred to the filter, the flask being freed from the residue of the fatty acids by several small quantities of hot water. It is essential that a few drops of water always remain under the acids on the filter. When all the acids are on the filter, all the water on the latter is removed by blowing away and the filter immediately placed carefully in the desiccator which is dried at 100° and weighed at the end of each hour. When the difference between two successive weighings is less than 1 mg., the weight of the fatty acids thus obtained, calculated for 100 grams of the substance, gives the insoluble fixed acid number sought.<sup>1</sup>

The insoluble fatty acid number varies little for most oils and fats, usually 0.5-0.65 for oils and 0.15-0.27 for fats. Some vegetable

The determination of the quantity of hydroxy-acids contained in a fatty substance is effected by Fahrion's method, based on the insolubility of the hydroxy-acids and the solubility of all the fatty acids, in light petroleum.

From 3 to 5 grams of the fatty substance are saponified in the usual way (*see* 5 : Saponification), the alcohol evaporated, the soap dissolved in 50–70 c.c. of hot water, decomposed in a separating funnel with dilute hydrochloric acid, shaken well with 100 c.c. of petroleum ether (boiling below 80°) and left until the two separate layers are perfectly clear. The aqueous layer is run off and then the petroleum ether, the insoluble hydroxy-acids, which remain adherent to the walls of the funnel, being washed several times with petroleum ether and afterwards dissolved in boiling alcohol. The alcoholic solution is evaporated to dryness in a tared dish and the residue dried at 100° and weighed.

This method allows of the determination of the hydroxy-acids produced by the oxidation, either natural or artificial, of an oil or fat. Such a determination has special importance in the analysis of boiled linseed oil and of the so-called blown oils, which are rich in hydroxy-acids.

## 16. Lactones or Internal Anhydrides

The simplest method of determining the content in internal anhydrides of a mixture of fatty acids is based on the following principle : in a mixture of pure insoluble fatty acids it is found that the acid number is equal to the saponification number, so that there is no ester number. If, however, the fatty acids are accompanied by lactonic anhydrides, the saponification number differs from the acid number. This is because the fatty acids are saturated immediately in the cold by potash, whilst the lactones must be boiled with excess of alcoholic potash in order to be neutralised.

Hence, to ascertain the content in lactones of a mixture of fatty acids, it is sufficient to determine by the ordinary methods the acid number and the saponification number and, consequently, the ester number. From the latter the content of lactone may be calculated, when the molecular weight from which the ester number is calculated is known (usually the lactone content is calculated as stearylactone).

In order that the acid, saponification and ester numbers of the fatty acids may not be confused with the respective numbers for the fatty substances, it has been proposed to call the former : *Constant acid number*, *constant saponification number* and *constant ester number*.

EXAMPLE : If a mixture of fatty acids gives the constant acid number 160 and the constant saponification number 195, the constant ester number



## 17. Determination of the Glycerine

The simplest method of determining if glycerine is present is to heat a little of the latter to boiling with a few crystals of bisulphate : in presence of glycerine, unpleasant, irritating odors are evolved, while a strip of filter-paper soaked in concentrated nitroprusside solution containing a little piperidine is dyed blue if placed in the mouth of the test-tube.

The glycerine in fatty substances may be determined *indirectly* : that in the saponification of neutral fats 1 mol. of glycerine corresponds with 3 mols. of potassium hydroxide (168.3 grams) : the calculation of the ester number (*see* 9, above) by 0.05466 also gives the glycerine content. This method is, however, only applicable when the substances contain higher alcohols, unsaponifiable substances, etc.

To determine the glycerine *directly*, the fatty substance is saponified in the ordinary manner (*see* 5 : Saponification), then neutralized by an acid, the fatty acids separated by filtration, and the glycerine in the aqueous filtrate determined by one of the methods given in this chapter for the quantitative analysis of glycerine.

## 18. Determination of the Solid and Liquid Fats

The fixed (or insoluble) fatty acids entering into the composition of fatty substances may be divided into two principal groups : the solid fatty acids belonging to the acetic acid series and represented especially by stearic and palmitic acids (sometimes also by arachic and lignoceric acids) and the liquid, unsaturated fatty acids belonging to the acrylic series and represented by the less hydrogenated series and represented especially by oleic acid and its isomers, also by linoleic, linolenic and ricinoleic acids.

The best method for separating these two groups of fatty acids is based on the insolubility of the lead salts of the solid acids, and the solubility of those of the liquid acids, in ether. Special methods serve for the separation of the individual solid acids and the individual liquid acids.

### 1. Separation and Determination of the Solid and Liquid Fats

For such separation Tortelli and Ruggeri's method is used. 20 grams of the fat are saponified in the usual way (see 5 : Saponification), the soap being dissolved in water and the solution acidified towards phenolphthalein with acetic acid. Meanwhile, 3 grams of a neutral lead acetate solution are heated in a conical flask to boiling. The liquid reaches the boil the soap solution is run into it in a test-tube, the liquid is heated to boiling. The solid fatty acids precipitate.

to the sides and bottom of the flask, while the liquid becomes clear. The whole of the liquid is then decanted off and the soap washed with three successive quantities of 200 c.c. of hot water ( $70-80^{\circ}$ ). The water is drained off, the beaker cooled, the last drops of water adhering to the soap removed by means of filter-paper, and 220 c.c. of ether added. The flask is well shaken and then fitted with a reflux apparatus and the liquid gently boiled on a water-bath for 20 minutes with occasional shaking and subsequently immersed in cold water ( $4-5^{\circ}$ ) for two hours. The clear ether is filtered into a separating funnel,<sup>1</sup> care being taken to let as little as possible of the undissolved soap fall into the filter. The residue in the flask is then heated for 20 minutes with a fresh quantity of 100 c.c. of ether under a reflux condenser and the flask afterwards stoppered and placed on one side immersed in cold water.

Meanwhile the filter is washed with a little very cold ether which is caught in the separating funnel containing the other filtrate. The well-covered filter is placed on one side, while the ethereal liquid in the separating funnel is vigorously shaken with 150 c.c. of 20% hydrochloric acid to decompose the lead soap of the liquid acids and then left to stand until the ether has collected at the surface in a clear layer. The lower aqueous layer, together with the precipitated lead chloride, is run off, the treatment repeated with 100 c.c. of hydrochloric acid, and the ethereal solution then washed three times with distilled water (150 c.c. each time). Finally, the bulk of the ether is distilled off and the last traces driven off on a water-bath while a current of carbon dioxide is passed.

The liquid acids thus obtained are weighed and calculated to 100 parts of the substance. These liquid acids, provided they are kept out of contact with the air, may be further utilised for the detection of cottonseed oil and sesamé oil (*q.v.*) and for the determination of the absolute iodine number (*see* 13, above).

The lead soap of the solid fatty acids, left undissolved in the flask immersed in cold water, is collected on the filter placed on one side, as mentioned above, and washed well with very cold ether and then introduced into a separating funnel where it is shaken with ether and hydrochloric acid as in the case of the liquid acids.

The ethereal solution of the solid fatty acids is distilled and the residue dried in an oven at  $100^{\circ}$  and weighed. For greater accuracy, the weight found may be increased by the quantity of solid acids (stearic and palmitic) corresponding with their lead soap remaining dissolved in the ether, knowing that 50 c.c. of anhydrous ether at the ordinary temperature dissolve 0.0074 gram of lead stearate and 0.0092 gram of lead palmitate; these amounts correspond with 0.0054 gram of stearic and 0.0065 gram of palmitic acid.

of the liquid acids soluble, in alcohol, and (2) that of *Fach* based on the insolubility of the solid fatty acids and their cold acetone; this solvent also serves to separate stearic acids from myristic and lauric acids.

The content of liquid and solid acids in a fatty substance deduced from the absolute and relative iodine numbers. If  $I$  the iodine number or that of the fat as such, and  $I_a$  the absolute or that of the liquid fatty acids extracted from the fat, 1 part iodine corresponds with  $\frac{100}{I_a}$  parts by weight of liquid acids (1 part corresponds with 100 parts by weight of liquid acids). With the iodine  $I$ , absorbed by 100 parts of the fat there correspond  $\frac{100 \times I}{I_a}$  parts of liquid fatty acids, this last fraction giving the percentage of liquid acids in the fatty substance.

When a mixture of palmitic, stearic and oleic acids along with the content of oleic acid may be calculated from the relative iodine numbers of the mixture, since it is known that the theoretical iodine number of stearic acid is 90.07. Thus, if  $I$  is the relative iodine number of the mixture,  $O$  the percentage of oleic acid sought,

$$O = \frac{100 \times I}{90.07} \text{ or } O = 1.1102I.$$

Lastly, it must be pointed out that, with mixtures of the acids named above, the content of liquid and solid acids may be determined by means of the solidification point of the mixture, use being made of the table (*see* Tallow and Stearine, 1).

**2. Determination of the Stearic Acid.**—The content of stearic acid in a mixture of fatty acids obtained by saponification of a fat may be determined by Helmer and Mitchell's method, which is based on the fact that stearic acid is very slightly soluble in alcohol at 0°, whilst the liquid acids are much more soluble and the liquid acids readily soluble.

From 0.5 to 1 gram of the fatty acids, if solid, or 5 grams if liquid, are dissolved in 100 c.c. of alcohol of  $D = 0.8183$  (94.4% alcohol saturated at 0° with pure stearic acid; the solution is then allowed to stand and filtered and the residue washed with alcohol saturated with stearic acid, working always at 0°; finally the stearic acid remaining is weighed.

This method is applicable especially to mixtures of stearic acid and oleic acids, which are the most common; with more complex mixtures it does not give satisfactory results.

more general case, of stearic and palmitic acids, the respective proportions of these two acids may be determined from either the acid number or the melting point of the mixture.

The following table of Mangold and Marazza gives the proportions of stearic and palmitic acids in a mixture of the two acids, on the basis of the acid number.

TABLE XLII

**Stearic and Palmitic Acids from the Acid Number**

Acid Number (mgrms. of KOH per gram of mixture).	100 parts of mixture contain		Acid Number (mgrms. of KOH per gram of mixture).	100 parts of mixture contain	
	Stearic Acid.	Palmitic Acid.		Stearic Acid.	Palmitic Acid.
197.50	100	—	208.86	45	55
198.50	95	5	209.95	40	60
199.50	90	10	211.06	35	65
200.50	85	15	212.18	30	70
201.50	80	20	213.30	25	75
202.50	75	25	214.45	20	80
203.50	70	30	215.60	15	85
204.60	65	35	216.77	10	90
205.60	60	40	217.95	5	95
206.70	55	45	219.13	0	100
207.77	50	50			

The following table gives the stearic and palmitic acids contained in a mixture of these two acids in relation to the melting point of the mixture, according to Heintz and according to Hehner.

TABLE XLIII

**Palmitic and Stearic Acids from the Melting Point**

Melting Point.		Solidifying Point.	Palmitic Acid. %	Stearic Acid. %
Heintz.	Hehner.			
62.0°	61.8°	—	100	0
60.1	59.0	54.5°	90	10
57.5	56.5	53.8	80	20
55.1	54.2	54.0	70	30

By unsaponifiable substances in fatty matters is usually understood substances which are not attacked by the alkali during the saponification, such as mineral oils, resin oils, solid paraffin and ceresine—very unsaponifiable in the strict meaning of the term—and also substances which are liberated by the saponification itself and separate owing to their insolubility under the conditions of saponification, such being, for example, the higher alcohols (ceryl and myricyl alcohols, cholesterol and

The latter substances form an integral part, i.e., enter into the constitution, of many fatty matters and waxes, while the former (mineral oils and the like) may be added artificially to fats.

To separate the unsaponifiable substances from fats it suffices to proceed in the usual way (*see* 5), to dissolve the soap in water and shake with ether or petroleum ether (b.pt. below  $80^{\circ}$ ), to separate the unsaponifiable and evaporate the ethereal solution, which will leave the unsaponifiable matters. To prevent emulsification, which often occurs when the soap is shaken with ether, a little alcohol may be added and a large quantity of ether used.

To determine quantitatively the unsaponifiable substances in fats, a convenient and accurate to work as follows:

20 grams of the substance to be examined are saponified by boiling with 15 c.c. of 50% caustic soda solution and 50 c.c. of alcohol. For about 30 minutes, the liquid being then transferred to a flask in which the alcohol evaporated, 8-10 grams of sodium bicarbonate (to neutralize the excess of caustic alkali into carbonate) and 70-80 grams of ether are being gradually mixed in. When the whole is quite dry it is pressed in a thick filter-paper thimble and extracted in an extraction apparatus with petroleum ether (b.pt. below  $80^{\circ}$ ). The solvent is subsequently evaporated, the residue, dried at  $100^{\circ}$  and weighed, giving the quantity of unsaponifiable matter.

The unsaponifiable matters which may be extracted from fats by this way or by the other methods given under particular cases (see 5). Detection of Phytosterol) are mainly as follows:

**1. Higher Alcohols.**—These are divided into those of the aliphatic series (cetyl, ceryl, myricyl) and those of the aromatic series (cholesterol, phytosterol). The former, which occur especially in waxes, melt at moderately high temperatures—cetyl alcohol at  $50^{\circ}$ , ceryl at  $55^{\circ}$ , and myricyl at  $85^{\circ}$ ; they are soluble in alcohol, from which they separate readily, and they dissolve in and combine with boiling acetone. The solution remaining liquid on cooling provided that a sufficient

solid acetyl compound which, when purified and recrystallised from alcohol, melts at  $114-115^{\circ}$ . If a solution of a little cholesterol in 2 c.c. of chloroform is shaken with an equal volume of concentrated sulphuric acid, the chloroform solution assumes a red coloration, which soon changes to cherry-red and then to violet-red, this persisting for some days, whilst the acid liquid turns reddish brown; if a few drops of the chloroform solution are shaken in a porcelain dish, the colour changes successively to blue, green and dirty yellow.

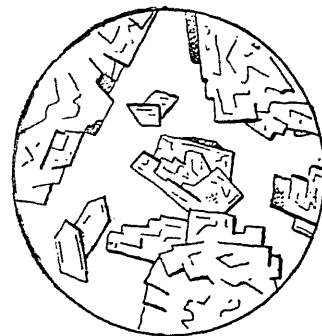


FIG. 54

*Phytosterol* or *sitosterol* (cholesterol from plants) occurs in fatty substances of vegetable origin. It dissolves in alcohol, from which it crystallises in tufts of broad, blunt-ended needles, having the microscopic appearance of elongated, blunted plates (Fig. 55), m.pt.  $135-144^{\circ}$ . When boiled with acetic anhydride, phytosterol also gives an acetyl-compound, m.pt.  $125-137^{\circ}$  (purified and recrystallised). With chloroform and sulphuric acid it behaves like cholesterol.

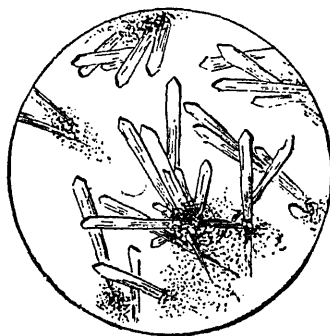


FIG. 55

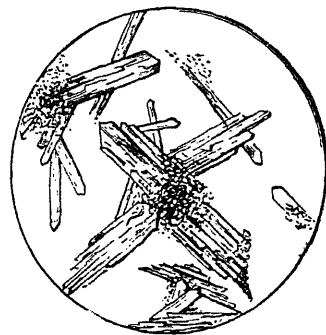


FIG. 56

When a mixture of cholesterol and phytosterol—which may be obtained from a mixture of animal and vegetable fats or oils—is crystallised from alcohol, the crystals show the predominant form of the phytosterol (Fig. 56) and melt at temperatures intermediate to the melting points of cholesterol and phytosterol (*see also* Lard).

**2. Paraffin Wax. Ceresine.**—These are solid and are insoluble in alcohol, aniline and acetic anhydride,<sup>1</sup> and hence distinguishable from the

## 20. Detection and Determination of the Resin

Resin (colophony) <sup>1</sup> is often found mixed with fatty substances (e.g., ally boiled linseed oil for varnishes and the like), waxes, and soaps.

**1. Qualitative Investigation.**—With neutral fats or oils or waxes, 5–10 grams of the substance are heated to boiling for a few minutes with as much 70% alcohol and the alcoholic liquid allowed to boil off and evaporated: the colophony, which is easily soluble in alcohol, remains as residue and is identifiable by its general characters and by one of the following reaction (Morawski's):

A small quantity of colophony, dissolved in 1–2 c.c. of acetone, is then treated with 1–2 drops of sulphuric acid of D 1.53 (concentrated sulphuric acid of 66° Baumé plus 35.7 c.c. of water), gives a transient red coloration.

A similar reaction is, however, given by cholesterol when, wool fat may be present. In such case the residue from the evaporation of the alcoholic liquid is taken up in dilute potassium hydroxide solution (which readily dissolves colophony), the liquid being shaken with ether (which dissolves cholesterol) and the aqueous alkaline liquid decanted. The resin acids thus obtained tested by means of Morawski's reaction.

With soap, about 5 grams are dissolved in water and the solution extracted with ether, the aqueous liquid being acidified and the fatty acids precipitated. The resin acids are then tested by Morawski's reaction.

**2. Quantitative Investigation.**—When mixed with fatty acids or with soaps, colophony may be determined by *Twitchell's method*. This is based on the fact that, in alcoholic solution, the acids of colophony are not esterified by gaseous hydrogen chloride, whilst fatty acids are. The colophony is converted into ethyl esters under these conditions. The procedure is as follows:

The mixture of fats and resin is saponified in the usual manner. The fatty acids then separated by acidifying the soap solution. The residue of a soap, this is dissolved in water and the solution filtered and acidified with acid. With mixtures containing unsaponifiable substances, necessary, after saponification, to extract the liquid with benzene or petroleum ether to remove the unsaponifiable matter, the aqueous solution is then decomposed with an acid. The fatty and resin acids then separated. They are well washed and dried and 2–3 grams dissolved in 50 c.c. of 70% alcohol and dry hydrogen chloride gas passed into the solution until the solution is about 10° by immersion in water and ice. The current of gas

(a) *Volumetrically.* The product of the esterification is dissolved in ether and washed repeatedly with water to eliminate the mineral acid and then diluted with 50 c.c. of neutral alcohol and titrated with N/10-potassium hydroxide in presence of phenolphthalein: 1 c.c. N/10-KOH = 0.0340 gram of resin.

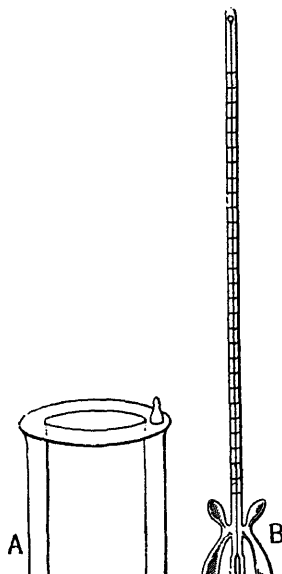
(b) *Gravimetrically.* The esterification product is dissolved in 50 c.c. of petroleum ether (b.pt. below 80°), shaken well, and the aqueous acid liquid separated. The petroleum ether solution is washed with water and shaken with 50 c.c. of an aqueous solution containing 0.5 gram of caustic potash and 5 c.c. of alcohol. The resin acids pass into the aqueous alkaline solution, whilst the fatty esters remain dissolved in the petroleum ether. The alkaline aqueous liquid is, therefore, separated and acidified, the resin acids thus obtained being removed by shaking the liquid with ether; the solvent is then evaporated and the residue dried at 100° and weighed.

This method gives only approximately exact results, which are more accurate with the volumetric than with the gravimetric method. Modifications have been suggested by Fahrion<sup>1</sup> and by Wolff and Scholtze,<sup>2</sup> but it is most commonly used in its original form. For more exact determinations, the method of Twitchell and Gladding may be used under the conditions laid down by Holde and Marcussen.<sup>3</sup> Another method for the determination of resin, based on the solubility of the alkali resins in acetone, has been proposed by Leiste and Stiepel.<sup>4</sup>

## 21. Maumené Number

This represents the rise in temperature produced when the fatty substance is mixed with concentrated sulphuric acid under definite conditions. Various methods of measuring this increase, based on the original one of Maumené, have been suggested. Nowadays suitable forms of apparatus are used (*thermo-oleometers*), such as that of Jean<sup>5</sup> or that of Tortelli.

Tortelli's *thermo-oleometer* consists of a small glass vacuum-jacketed vessel *A* (Fig. 57), and a thermometer-stirrer *B* provided with two glass vanes near the bulb. 20 c.c. of the oil are pipetted into *A*, stirred for a minute by rotation of the stirrer and the temperature read (*t*). By means of another pipette 5 c.c. of sulphuric acid (D exactly 1.8413) are allowed to flow on to the oil while the stirrer is





The Maumené number is  $t_1 - t$ .

To obtain constant and comparable results it is necessary always exactly as described and to use acid of the exact density be controlled by using 20 c.c. of distilled water in place of the 50 being then obtained by the test. The oil and acid used for some time (about 30 minutes) to attain the temperature of the air.

In the case of a drying oil, it is convenient to dilute it with olive oil of a known Maumené value, the result obtained being properly corrected.

Solid fats are used in the fused state, the acid being at the temperature; allowance is then made in the calculation for the specific heats.

The results obtained for drying and non-drying oils with Torricelli are about 8-10 higher than those given by Jean's apparatus.

The results vary with the method used for their determination, the nature of the substances themselves. In general, however, fish oils and fish-liver oils give values above 100, semi- and blubber oils, values less than 100 (usually 30-90), and animal oils (30-35).

Old or rancid oils and those which have been exposed to the air give values different from the fresh oils.

## 22. Drying Properties of Oils

Certain fixed oils, when exposed to the action of the air, gradually dry, forming transparent and elastic pellicles like those of resins. Oils which either remain fluid or form a thin little, even after long exposure to the air, are *non-drying* and thicken and dry, although incompletely and slowly, are termed *drying oils*.

The drying properties of an oil depend on its power to combine with greater or less rapidity, atmospheric oxygen, so that the dryness of an oil may be determined from the quantity of oxygen absorbed from the rapidity of the absorption.

There are several methods of determining the absorption, the common being those of Livache and Bishop.

1. LIVACHE'S METHOD. Precipitated lead is prepared by dissolving a sheet of zinc in 10% lead acetate solution acidified with nitric acid, washing the lead precipitate formed with water, alcohol and ether, drying it in a vacuum over sulphuric acid. A clock-glass with a hole in the middle of the lead on it is weighed and about 0.5 gram of the oil is placed in drops on to it, care being taken that the different drops

fining the solvent, drying the residue on a water-bath and powdering it. Of this resinate, 0.2 gram is heated in a water-bath with 10 grams of the oil to be tested until completely dissolved. 1 gram of precipitated silica and a glass stirring-rod are placed in a dish and the whole tared, 1.02 gram of the oil plus resinate being allowed to fall drop by drop on to the sand and the whole weighed. The mass is well mixed and left exposed to the air at the temperature 17–25° for drying oils or 20–30° for other oils. After 6 hours and after further successive intervals of 12 hours the basin is weighed (the mass being stirred each time) until of constant weight. The maximal increase of weight, multiplied by 100, Bishop terms the *degree of oxidation* of the oil.

Drying oils usually absorb oxygen easily and rapidly, so that after an exposure of 2–3 days the absorption is practically at the maximum attainable even after 8–10 days. On the other hand, non-drying oils do not increase in weight during the first days of exposure and begin to absorb a small quantity of oxygen only after 5–6 days.

According to Livache, the maximum amount of oxygen absorbed per 100 parts of linseed oil is about 14, the amounts for walnut oil, poppyseed oil, cottonseed oil and beechnut oil being 8–5. Olive, arachis, sesamé and colza oils absorb only 1–3% of oxygen.

According to Bishop's method, the mean degree of oxidation is 17 for linseed oil, 13–15 for hempseed, poppyseed and walnut oils, and 6–9 for cottonseed, sesamé and arachis oils.

## 23. Colour Reactions.

Different fatty substances, more particularly the fatty oils, give special colorations with various reagents, such as acids, alkalies and different salts. Some of these reactions serve to distinguish certain groups of oils, whilst others, being specific for a single oil, serve to characterise the latter. These specific reactions will be dealt with in the special part in the paragraphs treating of the particular oils (*see* Cottonseed Oil, Sesamé Oil). Some of the group reactions in more general use for the distinction of the different groups of vegetable oils (for animal oils, *see* Fish Oils) will be described here.

I. HEYDENREICH'S REACTION. Five or six drops of the oil are allowed to drop from a pipette on to about 5 c.c. of pure sulphuric acid (66° Baumé) in a flat-bottomed porcelain dish. In about three minutes the oil spreads to form a very thin layer on the acid; the colour formed during this time in the zone of contact between oil and acid is observed.

With olive, arachis and almond oils, there is no sensible change of colour, the oil remaining pale yellow or yellow, although sometimes with olive oil a greenish-yellow coloration appears. With very old or rancid oils, colours

tion after the mixture has been kept for 20 minutes in a boiling water-bath. Olive, almond, hazel-nut and arachis oils retain their color or become somewhat paler. Olive oil may, however, show a greenish tint, especially in the cold. If these oils are heated they turn orange-coloured.

Sesamé, cottonseed, beechnut, linseed, walnut, colza, and etc., change to orange or brownish red.

3. BRULLÉ'S REACTION. In a test-tube 10 c.c. of the oil, 1 c.c. of dry, finely powdered egg-albumin and 2 c.c. of pure nitric acid as for Hauchecorne's reaction are carefully and uniformly mixed. When the acid begins to boil, the whole being then shaken somewhat, the boiling is continued until the albumin is completely dissolved, this taking a few seconds.

During the boiling with the acid and albumin, olive oil is entirely decolorised and after cooling forms a more or less straw-yellow colour which persists for a long time, but on heating it sets to a solid mass of the same colour. Similar behavior is shown by arachis, almond and walnut oils.

Seed-oils, however, become deep yellow (colza, sesamé) and change to brown (cottonseed, poppyseed, maize, beechnut, linseed).

4. BELLIER'S REACTION. 5 c.c. of the oil or filtered oil and 5 c.c. of pure, colourless nitric acid of  $D = 1.4$  and 5 c.c. of a 1% solution of resorcinol in benzene are introduced into a graduated test-tube with a ground stopper and shaken for about 10 seconds, the color is observed during the shaking and immediately afterwards.

In place of the benzene solution of resorcinol, a 0.1% solution of phloroglucinol (*Kreis*) may be used.

Seed oils in general, and especially sesamé, cottonseed, linseed, maize (corn oil), soja-bean and colza oils, give colorations from pink to red to violet to brown (with phloroglucinol solution) or red).

This reaction serves more particularly to detect vegetable oils and fats (lard), in lard oil, in foot oils, and also in olive oil, since mineral oils and olive oil give no appreciable coloration, at any time. After this time all oils and fats give colorations.

Practice with oils and fats of known origin is necessary in order to distinguish pure oils and fats from mixtures by this reaction.

With oils which have been subjected to long exposure to light in the air, the reaction fails.

Drying oils give an orange-yellow or brown liquid product.

## SPECIAL PART

### Vegetable Oils

vegetable oils is meant those fatty substances extracted from the vegetable kingdom and liquid at the ordinary temperature. These oils are very numerous but only relatively few are in common use, these include olive, almond, arachis, colza, cottonseed, linseed, sesamé and castor oil which are treated in detail below. Table XLIV on p. 410 gives the physical characters of these oils and of the other more important vegetable

#### ARACHIS OIL

obtained from the seeds of *Arachis hypogæa*. It is pale yellow and has a slight greenish tinge and an agreeable taste. About 15 grams dissolve in 1000 c.c. of 70% alcohol at 15°.

With Heydenreich's, Brullé's and Hauchecorne's reagents it gives no characteristic colorations, only a pale pink colour being obtained with the latter at the cold. The other chief physical and chemical characters are given in Table XLIV.

A characteristic of arachis oil is its content of arachidic and lignoceric acids. The detection and, if required, the determination of these acids is necessary to identify the oil and to detect its presence (approximately also its quantity) in mixtures with other oils.

**Detection and Determination of Arachidic and Lignoceric Acids.**—The most convenient method for this purpose is that of Tortelli and Ruggeri (*see* below), which, like various other methods, is based on the same principle as Renard's older method.<sup>1</sup>

A preliminary and more rapid examination may be made by the other methods described below.

**TORTELLI AND RUGGERI.** 20 grams of the oil are saponified, the fatty acids separated, and the solid acids extracted from these by means of lead salts,<sup>2</sup> the operations being carried out exactly as described in the official method 18 (Tortelli and Ruggeri's method). The solid fatty acids obtained are placed in a suitable flask, 100 c.c. of 90% alcohol and a few drops of dilute hydrochloric acid (about normal) being added. The flask is closed with a stopper through which a thermometer passes into the liquid and the mixture is heated gently (not above 60°) on a water-bath and carefully

from pure arachis oil, the temperature at which crystals from the alcoholic solution cools is 35–38°. The melting point of acids obtained in this first crystallisation is usually

No other oil gives a crystalline precipitate in such when the alcoholic solution of its solid acids (prepared as above) is cooled to the ordinary temperature. Only cottonseed oil and some Tunisian olives give a precipitate, but this is amorphous. In perfectly opaque mammillary masses, m.p. below 70°, no precipitate does not form in a second crystallisation.

If it is required to estimate exactly the *quantity* of lignoceric acids, the crystals formed in the alcoholic solution are washed with three successive quantities of 10 c.c. of 70% alcohol, then thoroughly with 70% alcohol. The crystals are then dissolved in 100 c.c. of 90% alcohol (or a less volume if the amount of acid is small) and the crystallisation repeated as described above. The crystals are collected on a filter, washed twice with 10 c.c. of 90% alcohol, then with 70% alcohol until this dissolves no more; they are then washed with a little boiling absolute alcohol, the solution being evaporated in a dish and the residue dried at 100° for about an hour. The weight found is added that of the arachidic and lignoceric acids in solution in the 90% alcohol used for the various washings, the following solubility coefficients (Tortelli and others) are employed:

Weight of Acid obtained in grams.	Number of grams dissolved by 100 c.c. of 90% alcohol at temperature of	
	15°	17.5°
1.00 or more . . . . .	0.071	0.081
0.70 . . . . .	0.068	0.078
0.50 . . . . .	0.064	0.075
0.25 . . . . .	0.052	0.060
0.05 or less . . . . .	0.031	0.040

Arachis oil contains, on the average, 4.80% of arachidic and lignoceric acids together, so that the proportion of these acids found by analysis indicates if the oil is pure or not. Further, the presence and relative amounts of these acids serve for the characterisation and determination of arachis oil with olive and other oils. In such mixtures, the crystallisation of arachidic and lignoceric acids from the alcoholic solution of the solid acids takes place at lower and lower temperatures as the proportion of arachis oil increases.

the temperature at which the first crystals form :

Temperature of precipitation of arachis oil . . .	35-38°	31-33°	28-30°	25-26°	22-24°	20-22°	18-20°	16-17°
Proportion of arachis oil . . .	100%	60%	50%	40%	30%	20%	10%	5%

The proportion of arachis oil in a mixture may, however, be determined exactly from the quantitative determination of the arachidic and lignic acids, the content in the pure oil being 4.80%. In this way as little of arachis oil in admixture with other oils may be detected.

**BELLIER'S METHOD (modified).**<sup>1</sup> Into a conical flask of about 100 capacity are pipetted 1 c.c. of the oil and 5 c.c. of about 8% alcoholic potassium solution (80 grams of pure potassium hydroxide dissolved in 100 c.c. of water and made up to 1 litre with 90% alcohol). The flask is heated with a stopper carrying a tube 80 cm. long (to avoid loss of alcohol) placed on a boiling water-bath with continual shaking until saponification is complete (4-5 minutes). The liquid is then cooled to about 25° and shaken with 1.5 c.c. (exactly) of dilute acetic acid (1 vol. of glacial acetic acid + 2 vols. of water), 3 drops (not more) of glacial acetic acid and 10 c.c. of 70% alcohol. If the liquid becomes turbid (as usually happens when this oil is present in marked quantity), it is gently heated until clear, the flask being then closed with a stopper through which passes a thermometer with its bulb in the liquid. The flask is then cooled and shaken in a water-bath so that the temperature of the liquid becomes exactly 16°, at which it is maintained for 5 minutes with gentle shaking.

If the liquid remains clear it is kept at 15.5° for 5 minutes, and if it still remains clear, arachis oil is either absent or present in less proportion than 5%. The appearance of turbidity at 15.5° indicates the presence of arachis oil (about 5%) in the oil. With higher proportions, marked turbidity appears even at 16°. With pure arachis oil, the liquid begins to show turbidity at about 40°.

The temperature at which the alcoholic solution of the fatty acids, obtained as described above, first becomes turbid serves to indicate approximately the proportion of arachis oil in its mixtures with olive oil :

		Temperature at which turbidity appears.
Pure olive oil . . . . .		11.5-14.5°
„ „ + 5% arachis oil . . . . .		16-17
„ „ 10 „ . . . . .		19-20
„ „ 20 „ . . . . .		25-26
„ „ 30 „ . . . . .		29-30
„ „ 40 „ . . . . .		31-32
„ „ 50 „ . . . . .		33-34
„ „ 60 „ . . . . .		35-36

then decomposed with a dilute acid to liberate the fat dissolved in petroleum ether. The solution is filtered and the arachidic and lignoceric acids investigated by precipitation in alcohol in the manner of the Tortelli and Ruggeri method.

**2. Detection of Adulterations.**—Commercial arachis oil adulterated with, or may contain as impurities, sesamé oil, poppyseed and other seed oils. Sesamé and cottonseed oil are detected by the reactions of Villavecchia and Fabris and of Hauchecorne (see Colza Oil and Cottonseed Oil), colza oil by Tortelli and Forster, and by a lowering of the saponification number (see Colza Oil and other seed oils in general by the colour reaction of Hauchecorne, and Brullé, and by a diminution in the iodine number and lignoceric acids.

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*Comestible arachis oil*, when fresh, should contain only 1% of free acid. Old oils and those for industrial use are more or less acid and contain up to about 30% of free acid (calculated as oleic acid), the usual amount being about 20%. *Arachis oil for soapmaking* should contain not more than 1% of moisture and foreign matters together and should have an iodine number 87–100, solidification point of the fatty acids 5–6° (Tortelli) 50–6.

The following products are also sold: *Arachis margarine*, produced by pressing the oil in the cold (m.pt. 22–25°, iodine number 70–75), produced by purifying the rancid oil with soda and compounds of soda, neutral oil and various impurities; and *arachis oil No. 2*, obtained by saponification of rancid oils with ammonia. The commercial value of the oil No. 2 depends on the content of total fatty matters (Tortelli, 1, A and C).

## COLZA OIL AND OTHER CRUCIFEROUS OILS

The more common oils of the Cruciferae are colza oil, rapeseed oil, less common are those of jambo, turnip, mustard (white mustard seed and hedge mustard. All have very similar characters.

Colza oil and rapeseed oil (from the seeds of *Brassica napus*), which are most used, are yellow, sometimes tend to be green, have a special, more or less pronounced odour and a bitter taste. About 8 grams dissolved in 1000 c.c. of absolute alcohol give the following characters are given later in Table XLIV.

With Heydenreich's reagent they give orange coloration, with apparent brown striæ, especially if the oil is containing dissolved matters. With Hauchecorne's and Brullé's reagents they give more pronounced colorations.

tioned above, are their low saponification number (*see* Table XLIV) and their content of erucic acid. By the determination of the saponification number and essentially by certain tests on the fatty acids these oils may be identified and their presence in mixtures with other oils detected. These tests are as follows.<sup>1</sup>

**The Tortelli and Fortini Tests on the Fatty Acids.**—These include the determinations of the melting point and iodine number of the solid fatty acids and the critical solubility temperature of the sodium salts of the liquid acids, these characters being especially influenced by the presence of erucic acid. The solid and liquid fatty acids should first be prepared (*see a*) and the determinations indicated then made (*see b* and *c*).

*a) Preparation of the solid and liquid fatty acids.* 20 grams of the oil are saponified with alcoholic potash and the potassium soap converted into the lead soap by the Tortelli and Ruggeri method (*see* General Methods, p. 100). The lead soap, dried with filter-paper, is taken up with 80 c.c. of ether, shaken well, heated for 20–30 minutes in a reflux apparatus with occasional shaking and then cooled in water at 15° for an hour. The ethereal solution is subsequently decanted through a filter into a separating funnel, as little as possible of the solid residue being introduced on to the filter. The residue is heated with 40 c.c. of ether in a reflux apparatus for 20 minutes, cooled at 15° for an hour, and the whole then collected on the filter, the ether passing into the separating funnel. The flask and residue are washed with 40 c.c. of ether. This washed lead soap, insoluble in ether, is introduced into another separating funnel by perforating the filter and washing with ether, of which 100 c.c. are used.

To each separating funnel 150 c.c. of 20% hydrochloric acid are added, the funnel being thoroughly shaken and then left at rest until the ethereal solution has separated well, the aqueous liquid and the lead chloride formed being run off. This treatment is repeated with a second quantity of 100 c.c. of hydrochloric acid and if necessary with a third quantity. The two ethereal solutions are then washed twice with 100–150 c.c. of water, care being taken not to shake too vigorously. The ethereal solutions are finally passed through two pleated filter-papers into two glass dishes, from which the solvent is evaporated at as low a temperature as possible. In one dish the solid acids (from the lead salts insoluble in ether) and in the other the liquid acids of the oil remain.

*b) Tests on the solid acids.* The *melting point* is determined with a test tube (*see* General Part, 4) and is taken as that temperature at which the substance falls into the lower part of the bulb. The *iodine number* is determined by Hübl's method.



being heated gently, treated with slight excess of saturated sodium carbonate solution, evaporated almost to dryness and dried over sulphuric acid. The dry residue is powdered and purified by treatment with admixed sodium carbonate by successive treatments with 10 c.c. of absolute alcohol, with which it is heated to boiling. The liquids are filtered hot and the sodium soap separated by filtration as a white or straw-yellow, caseous mass, which is pumped on a vacuum over sulphuric acid. Of the perfectly dry, powdered soap 0.5 gram is treated in a large test-tube with 20 c.c. of absolute alcohol, the tube being hung in a beaker full of water and a thermometer in it, so that its bulb is in the centre of the liquid.

The liquid is then heated and continually stirred with a glass rod until a clear solution is obtained, the whole being then allowed to cool spontaneously. At a certain point the alcoholic solution is seen to contain minute crystals, which are only barely perceptible but rapidly multiply and fill the whole mass of the liquid. The temperature at which the first crystals are observed is the characteristic crystallisation temperature.

When the crystallisation is well under way, the thermometer remains stationary for some time, or at least falls with great slowness.

The sodium soap of the liquid fatty acids of colza oil has a solubility temperature in alcohol, 50–45°; for other seed oils a solubility temperature is lower (*see later*). Further, the sodium soaps of various seed oils are deposited with a caseous, flocculent appearance, whereas that of olive oil, at least at first, is distinctly crystalline.

From the melting point and iodine number of the solid sodium soap the critical solubility temperature of the sodium soap of the liquid (olive or rapeseed) oil may be detected and approximately estimated for other oils; the following data are given by Tortelli and

Oils.	Melting Point of Solid Acids.	Iodine Number of Solid Acid
Colza oil . . . . .	41–42°	62
Olive oil . . . . .	58–59	7·5
Colza oil, 50 } . . . . .	47–48	32
Olive oil, 50 } . . . . .	48–49	28
Colza oil, 30 } . . . . .	50–51	22
Olive oil, 70 } . . . . .		
Colza oil, 20 } . . . . .		

mixed with olive oil (*q.v.*) and, in their turn, may be adulterated with other seed oils (linseed, poppyseed, cameline, hempseed, etc.), and particularly with fish oils and oils of other marine animals, as well as with mineral oils.

The determination of the various characters (especially saponification, iodine and Maumené numbers) and the test for erucic acid by Tortelli and Fortini's method readily show if the oil is pure or otherwise. Seed oils in general and animal oils raise the saponification number, while linseed, hempseed and poppyseed oils raise also the iodine and Maumené numbers. Fish oils and other marine animal oils are detected by means of the test for the octabromo-compounds and the Tortelli and Jaffe reaction (*see* Fish Oils), and mineral oils by testing for unsaponifiable substances.

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*Colza oil for comestible and illuminating purposes* should be well refined and not acid. *Industrial ravisson oil* should have:  $D = 0.911-0.937$ , iodine number  $= 103-108$ , saponification number  $= 175-178$ , refractive index (Zeiss) at  $25^{\circ} = 68-71$ , Maumené number (Tortelli)  $= 60.8^{\circ}$ .

## COTTONSEED OIL

Obtained from the seeds of *Gossypium herbaceum*. It is yellow or golden-yellow or, if not well refined, slightly reddish-yellow; it has characteristic but not very pronounced smell and taste. About 18 grams dissolve in 1000 c.c. of absolute alcohol at  $15^{\circ}$ . The other physical and chemical characters are indicated in Table XLIV.

Heydenreich's reagent gives a deep orange, and Hauchecorne's or Brullé's reagent a reddish-brown, coloration with the oil. The latter also gives the following characteristic reactions:

**1. Milliau's Reaction, modified by Armani.**—10 grams of the oil are saponified in the usual way, the soap being dissolved in water and the solution shaken in a separating funnel with 100 c.c. of ether and 30 c.c. of 10% hydrochloric acid. After standing, the acid aqueous layer is removed and the ethereal solution of the fatty acids washed by shaking several times with water until the latter no longer gives an acid reaction. The ether is then evaporated, the fatty acids thus obtained being dissolved in 15 c.c. of 90% alcohol (puriss.)<sup>1</sup> and the solution mixed with 1-2 c.c. of alcoholic silver nitrate solution and heated in a water-bath at  $80-90^{\circ}$ .

Pure cottonseed oil gives an intense brown coloration almost immediately and then also a black precipitate. Mixtures of oils or fats containing cottonseed oil yield a violet-brown coloration which, after a few minutes' heating,

<sup>1</sup> This reaction and in general all reactions with silver nitrate require the use of

tion appears after 5-10 minutes of heating, whilst with oil from cottonseed oil no sensible coloration is ever formed.

**2. Milliau's Reaction, modified by Tortelli and Ruggeri's lead-salt method** (*see* General Methods, 18, 1) and dissolved in a test-tube in 10 c.c. of 90% alcohol (puriss.), thoroughly mixed with 1 c.c. of 5% aqueous silver nitrate, heated in a water-bath at 70-80°.

With pure cottonseed oil the liquid assumes almost a reddish coloration which soon turns to reddish-brown, the liquid becoming turbid and appearing violet-blue in transmitted light after 5-10 minutes heating. With oils and fats quite free from lead no coloration is obtained even after heating for half an hour. Mixtures containing only 1% of cottonseed oil, a deep brown coloration appears.

**3. Halphen's Reaction.**—According to the most reliable method by the author,<sup>1</sup> this test is carried out as follows: In a test-tube 1 c.c. of the oil and 2 c.c. of sulphocarbon reagent are mixed, dissolving 1 gram of powdered, refined sulphur in 100 c.c. of carbon disulphide and then diluting with 100 c.c. of amyl alcohol. The mixture is shaken to the extent of two-thirds in a salt solution and heated in a water-bath for 1 hour, 2 c.c. of the same reagent being then added and the mixture heated for 30-40 minutes. In presence of cottonseed oil, a red coloration appears—according to the proportion of cottonseed oil (down to about 1% as a minimum)—appears more or less distinct.

Water hinders the reaction, so that the test-tube should be dried and the reagents and oil anhydrous; the latter is filtered through a dry filter.

Some cottonseed oils which have undergone special treatment show in place of a decided red coloration, a brown tint with an orange tinge, well seen by looking through the whole depth of the liquid.

With green or greenish olive oils containing little cottonseed oil the result is uncertain; in such cases it is well to decolorise the oil before using it at about 50° with animal charcoal and filtering at the same temperature.

**4. Halphen's Reaction, modified by Gastaldi.**—The oil, containing 5 c.c. of the oil, 1 drop of pyridine and 4 c.c. of carbon disulphide is heated in a boiling water-bath for 30-60 minutes. In presence of cottonseed oil a red, pink coloration—according to the amount of the cottonseed oil—appears with Halphen's reagent; the colour is more distinct and the liquid is more turbid and is visible even with 0.5% of cottonseed oil.

is, however, of little practical value, since cottonseed oil treated in this way is scarcely utilisable, at any rate for mixing with comestible olive oil.

It is also to be noted that kapok and baobab oils give the same reactions as cottonseed oil, both with silver nitrate and with the carbon disulphide reagent, but even far more intensely (with silver nitrate the reaction occurs even in the cold and with Halphen's reagent, 1% of kapok oil mixed with other oil gives almost the same coloration as pure cottonseed oil). Kapok oil may, according to Milliau,<sup>1</sup> be distinguished from cottonseed oil by means of the action of silver nitrate on the fatty acids in the cold; but actually the fatty acids of cottonseed oil also slowly reduce silver nitrate in the cold and, in the case of mixtures, the reaction may be due as much to a little kapok oil as to a large amount of cottonseed oil. For a more certain indication other data must be employed. For instance, with mixtures of olive and arachis oils, the iodine number and other constants will show if the proportion of the extraneous oil is large or small. Thus, an arachis oil which gives Halphen's reaction as sharply and intensely as pure cottonseed oil but has a normal iodine number and a normal content of arachidic and lignoceric acids cannot possibly contain an amount of cottonseed oil capable of giving such an intense colour reaction; it is, therefore, more probable that such an oil is contaminated with a little kapok oil than with much cottonseed oil.

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*Comestible cottonseed oil* should show little colour and no unpleasant smell or taste and no acidity. The *industrial oil* should have:  $D = 0.922-0.930$ , iodine number = 103-110, solidification point of the fatty acids =  $32-40^{\circ}$ , Maumené number (Tortelli) =  $78.8^{\circ}$ .

*Refinery residues of cottonseed oil (soapstock)*, which are pasty and brownish-yellow to black, are valued on the basis of their total content of fatty matter (standard 50%), for the determination of which, see General Part, 1, A-C.

*Cottonseed margarine or stearine* is the solid part which separates on cooling the oil and is recovered from the latter by pressure at  $10-11^{\circ}$ ; it is white or yellowish, has the consistency of butter (m.p.  $16-32^{\circ}$ ) and gives the same colour reactions as cottonseed oil. Its specific gravity at  $100^{\circ}$  is  $0.864-0.868$ , saponification number 194-195, iodine number 95-96. Its value depends on the titer (solidifying point of the fatty acids; see Tallow) and on the content of total fatty matter (see General Part, 1, A-C).

## LINSEED OIL

Ordinary or crude linseed oil (for boiled linseed oil, see next chapter: Industrial Products of the Treatment of Fatty Matters), from the seeds of *Linum usitatissimum*, is yellow or brownish-yellow and has a peculiar odour and an unpleasant taste. It dissolves in about 40 parts of cold or 5 parts of boiling absolute alcohol. It contains a certain quantity of unsaponifiable substances (1-1.3%). Its physical and chemical characters are given in Table XLIV.

### 1. Reaction of the Hexabromo-compounds.—

shaken in a stoppered cylinder with 100 c.c. of a mixture of acetic acid, 4 vols. of nitrobenzene and 1 vol. of bromine (*Reagent*), 5 c.c. of the oil give a yellow precipitate composed of compounds of linolenic acid. This precipitate is soluble in chloroform and melts undecomposed at 175–180° (difference from oils of *see Fish Oils*).

Drying walnut and hempseed oils behave like linseed vegetable and animal oils (excepting those of marine origin) and give a precipitate or only a slight turbidity with the bromine reagent.

**2. Drying Properties.**—Linseed oil, being a drying oil, absorbs oxygen, its drying power increasing with the rapidity with which it absorbs its maximum proportion of oxygen. Under the conditions of the standard method (*see General Methods*, 22, Drying Properties of Oils), linseed oil absorbs about 14% of oxygen in two days, while by the maximum is 17% and is reached in 24 hours.

**3. Detection of Adulterations.**—Linseed oil may be detected by its reaction with other vegetable oils (especially colza, cottonseed, sesame, cameline, hempseed and other drying oils) or with animal oils, which are tested for as follows:

**1. OTHER VEGETABLE OILS.** Marked addition of other vegetable oils (especially if non-drying) to linseed oil generally lowers the iodine number and the Maumené number and a linseed oil with an iodine number above 165 and a Maumené number less than 120° is to be suspected. For example, colza oil may be detected by the Tortelli and Fournier test, cottonseed oil by the Halphen and the silver nitrate reactions, and sesame oil by the furfural reaction (*see these oils*). The presence of adulterations (such as colza, cottonseed, cameline and the like) is moderately difficult to ascertain, as these oils do not possess special colour reactions.

**2. FISH AND OTHER MARINE ANIMAL OILS.** The presence of these oils may be detected by the Halphen and Marcusson octal test, the iodine number, the Maumené number and the Tortelli and Jaffe colour reaction (*see Fish Oils*).

**3. MINERAL OILS.** These are detectable by the fact that they do not increase the density, the iodine number and the saponification number. They may, in addition, be tested for in the unsaponifiable matter (*see General Methods*, 19, Unsaponifiable Substances).

**4. RESIN OILS.** These may be recognised by the odour, the reaction with sulphuric acid (*see Resin Oils*) and by the fact that they are optically active (linseed oil is almost inactive, whereas resin oils are optically active and rotatory); further, they increase the density and lower the saponification number.

This is obtained from the seeds of *Amygdalus communis* or ordinary almonds, the sweet and bitter varieties giving oils very similar in all their properties. Almond oil is yellow or golden-yellow and about 16 grams of it dissolve in 1000 c.c. of absolute alcohol.

With Heydenreich's, Hauchecorne's and Brullé's reagents it remains pale yellow or becomes somewhat paler. The characters of the oil are given in Table XLIV and are determined by the methods already described.

**Detection of Adulterations.**—Almond oil may be adulterated with various seed oils (arachis, colza, cottonseed, walnut, sesamé, etc.), but especially with peach-kernel, apricot-kernel and plum-kernel oils. To detect such admixtures, the various characters must be determined (especially solidifying points of the oil and of the fatty acids, saponification and iodine numbers, Maumené number) and certain colour tests made (see below, 2).

The different extraneous oils may be detected as follows:

1. ARACHIS, SESAMÉ, COTTONSEED, COLZA, ETC. The first is detected by the arachidic and lignoceric acids, the second by the furfural reaction, the third by the Halphen reaction, and colza oil by tests on the fatty acids (see the respective oils). The presence of other seed oils in general (excluding those dealt with in 2) may be recognised by the colour reactions of Heydenreich, Hauchecorne, Brullé and Bellier (see General Methods, 23), to which almond oil does not sensibly respond.

2. PEACH-KERNEL, APRICOT-KERNEL AND PLUM-KERNEL OILS. These oils are commonly used as adulterants or substitutes for almond oil. They do not alter the characters of almond oil appreciably, excepting that apricot-kernel oil somewhat increases the Maumené number (50–51 for almond oil and 60–70° for apricot-kernel oil). The two following reactions serve for their detection.

**Bieber's reaction.** Equal volumes of pure sulphuric acid of 66° Baumé concentrated nitric acid (D 1.42) and water are mixed, one vol. of such mixture being then shaken with 5 vols. of the oil in the cold. Pure almond oil forms a yellowish emulsion which becomes reddish only after some time. Apricot-, peach- and plum-kernel oils form emulsions of a transient purple colour, which soon changes to deep orange and then to brown.

**Reaction with nitric acid.** 1 c.c. of fuming nitric acid, 1 c.c. of water and 2 c.c. of the oil are shaken vigorously at a temperature of about 10°: pure almond oil yields a whitish emulsion which, in two or at most six hours, sets to a solid mass of compact white granules with a little colourless, supernatant liquid. In presence of apricot- or peach-kernel oil the emulsion becomes coloured almost immediately, more or less reddish.

D = 0.914–0.920, iodine number = 94–100, saponification number = 180–185, and should be incongealable at  $-10^{\circ}$  and should respond to the test with nitric acid.

## OLIVE OIL

This is obtained from the fruit of *Olea europea*, and is sometimes greenish and with characteristic smell and taste. Grams of the oil dissolve in 1000 c.c. of absolute alcohol at  $15^{\circ}$ .

With Heydenreich's, Hauchecorne's, Brullé's or Belli's test gives a pale-yellow or greenish coloration, excepting with rancid oils, which yield more or less deep orange tints. The tests for the oil are given in Table XLIV.

Olive oil may be adulterated with various seed oils, such as arachis, cottonseed, sesamé, colza, ravisson or soja-bean oil, and with maize, poppyseed and other oils. Adulteration with la mineral oils has been observed, but only in exceptional cases.

**1. Tests and Determinations.**—Analysis of olive oil for the purpose of ascertaining the quality and purity, includes mainly the following:

(a) Examination of the objective properties, that is, the appearance (clarity, opacity, colour, smell and taste. The odour is brought out by rubbing a few drops of the oil between the hands and smelling them). The odour and taste indicate the fineness of an oil, its state of purity, and, with much practice, its purity.

(b) Determinations: solidifying point of the oil and the solidifying points of its fatty acids; the specific gravity; the refractive index on the Zeiss butyro-refractometer at  $25^{\circ}$ ; the Maumené index; the free acid, acid, saponification and iodine numbers. All these are made as described in the general part of the present chapter (except the refractive index, for which see Butter, Vol. II).

(c) Elaidin test (see General Methods, 24).

(d) The arachidic and lignoceric acid test and the Tottoli test for erucic acid (see Arachis Oil and Colza Oil).

(e) The colour reactions of Heydenreich, Hauchecorne, Milliau, Halphen, and Villavecchia and Fabris (see General Methods, also Cottonseed Oil and Sesamé Oil).

(f) With industrial olive oils, determinations of the moisture and extraneous impurities are necessary (see General Methods, 24), sometimes required to ascertain if the oil has been extracted with disulphide (see later, 8).

**2. Detection of Extraneous Oils.**—The various forms of

... the specific gravity, the melting and solidifying points of the fatty acids, the Maumené number, the refractometric value and the iodine number.

**SESAME OIL :** by the Villavecchia and Fabris reaction (*see* Sesame Oil); it alters the different characters in the same sense as does cottonseed oil.

**OTHER SEED OILS IN GENERAL :** by the general colour reactions already indicated (*see e*, above) and by certain alterations in the characters of the oil.

**ANIMAL OILS :** by the smell and by testing for cholesterol as indicated above (olive oil scarcely contains traces of phytosterol). Fish oils and oils of other marine animals are detected by the Tortelli and Jaffe reaction (Fish Oils).

**MINERAL OILS :** by the lowering of the saponification number and by examination of the unsaponifiable part (*see* General Methods, 19).

**Detection of Sulphocarbon Oil.**—200 grams of the oil are vigorously shaken with 50 c.c. of 90% alcohol and distilled from a water-bath, the distillate being collected in a flask containing a few c.c. of alcoholic potash solution (1 : 10) (recently prepared from the purest alcohol) and immersed in cold water. When about two-thirds of the alcohol added to the oil are collected, the distillation is interrupted. The distillate is then acidified with dilute acetic acid and treated with 1-2 drops of dilute mercuric sulphate solution: in presence of potassium xanthate (formed by the action of the carbon disulphide, distilled with alcohol, on the alcoholic potassium hydroxide), a brown coloration is formed and then a yellow precipitate of mercuric xanthate.<sup>1</sup> The presence of carbon disulphide in the oil is hence proved.

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Genuine *comestible olive oil* should have the following characters :

It should be clear and have the normal odour and taste.

**Solidifying point :** it should begin to become turbid at about 10°, and as the temperature falls it sets to a semi-solid mass between 6° and 2°; at 0° it forms a soft solid.

**Melting point of the fatty acids :** 22-28°.

**Solidifying point of the fatty acids :** 24-21°.

**Specific gravity at 15° :** 0.914-0.919.

**Reading on Zeiss butyro-refractometer at 25° :** 62-63. With oils which are unadulterated or altered, or obtained from bad olives, or washed or extracted with carbon disulphide, the reading may be as low as 60.

**Maumené number (Tortelli) :** 41-47° (44° may be taken as the mean). With

**Mean thermo-oleometer :** 32-39°.

**Acid number :** 2 at the most.

**Saponification number :** 185-196 (normally 192-195).

**Iodine number :** 79-88. Most commonly the iodine number is 80-83, only in oils from Liguria and Spain, and more often the oils of Crete, Tunis,



animal oils.

In general, an olive oil may be regarded as pure when : it is pale yellow by Heydenreich's, Hauchecorne's or Brullé's reaction ; saponification number not less than 192 and an iodine number not exceeding 83—does not contain arachidic, lignoceric or erucic acid. An oil with a saponification number less than 192 and an iodine number above 83—within the limits indicated in Table XLIV—but of normal behaviour in all the other tests, may be regarded as genuine.

The official Italian methods give for olive oil the limits of variation for the different characters, excepting that the solidifying temperature is as  $2-6^{\circ}$ , the refractometer reading at  $25^{\circ}$  as between 62 and  $62.8$ , the saponification number as 79-90. They give further : Reichert-Meissl number, 18-20 ; acid number, 95.5-96.2 ; acetyl number, 4-10 ; absolute iodine number, 80-83 ; unsaponifiable residue, which should be constituted of minimum 0.5% phytosterol scarcely sufficient for the reaction with chloroform ; free fatty acid (100 grams of the oil yield 0.45-0.47 gram of crude phytosterol) ; sesame and cottonseed oils give respectively 1.28 and 1.20 grams.

The *industrial oil for lighting or lubrication* should answer the requirements indicated for the genuine comestible oil. In some cases, however, a mixture of seed oils (arachis, colza or raven) are allowed, e.g., by the Italian Railways. It should not contain more than 1% of free acid (calculated as monohydrated sulphuric acid), should not congeal above  $-5^{\circ}$ , should not be adulterated with animal, mineral or resin oils, and should not contain any gummy or liginous substances or suspended foreign matters. Further, for lighting purposes should satisfy definite requirements with regard to burning, the illuminating power, etc.

*Industrial olive oil for soap-making* occurs in various qualities.

*Washed oil*, obtained by washing the olive residues (sanse) with water, contains impurities up to 2% ; free from sulphur ; acidity variable (100 grams yield 0.5-1.0 grams acid).

*Huile lampante* (yellow and green), obtained by filtering the oil, contains moisture and impurities up to 1%.

*Olive oil grease* or residues from the filtration of the washed oil, should be free from sulphur, unbleached and not treated with acid. Its composition is : on its content in total fatty matter—to be determined directly—calculated as fatty acids (exclusive of hydroxy-acids)—to be determined by saponification, the grease and separating the total fatty acids.

*Sulphur or sulphocarbon olive oil*, which is distinguished from the others by its saponification number not less than 180, acidity (as oleic acid) not exceeding 1%, moisture and impurities up to 2% and hydroxy-acids up to 3%.

## CASTOR OIL

From the seeds of *Ricinus communis*, is almost colourless, thick, dense and viscous, with characteristic smell and taste. It is soluble in alcohol in all proportions and in acetic acid in the cold. It is almost insoluble in petroleum ether and in vaseline oil, whilst

Castor oil is readily distinguished from other oils by its solubility in alcohol and its insolubility in mineral oils, by its specific gravity, acetyl number, viscosity and rotatory power, which are considerably higher than those of other oils. Its viscosity (Engler) at 50° is about 16 (water at 20 = 1) and its rotation in a 20 cm. tube at the ordinary temperature + 8° to + 9° (near degrees).

When prepared recently and in the cold, it is neutral, but it easily becomes acid. Old oils and those extracted in the hot or by solvents are more or less acid (up to more than 20% of free acids, as oleic acid).

The following tests are usually made :

**Solubility.**—This serves to show if the oil is pure or not, and is carried out as follows :

*Finkener's test.* 10 c.c. of the oil and 50 c.c. of 90% alcohol are shaken together : if the mixture is turbid and remains so at 20°, the castor oil is not pure.

*Morpurgo's test.* 1 vol. of the oil and 3 vols. of oil of vaseline are shaken together at 10–15° : after standing, the oil of vaseline separates from its original volume if the castor oil is pure, but with an increased volume if extraneous oils are present.

**Detection of Adulterations.**—(a) VARIOUS VEGETABLE OILS. Castor oil is rarely adulterated with vegetable oils (cottonseed, sesame, linseed, etc.), which may in any case be easily detected, since they differ from castor oil in the specific gravity, acetyl number and rotatory power and raise the saponification number (excepting colza or raven oil).

**CROTON ELLIOTIANUS OIL.** This oil does not greatly alter the color of litmus and is difficult to detect, especially if only in small proportion. The detection of its presence may, however, be obtained by boiling the oil with a very concentrated potassium hydroxide solution : on cooling, a thick, soapy mass is obtained with pure castor oil, and a yellow or brown mass in the presence of croton oil (1% or more).<sup>1</sup>

**Test for Resinous Substances.**—To ascertain if a sample of castor oil is contaminated with resinous substances or has been extracted in the presence of resinous substances, the following test, prescribed by the official Italian pharmacopœia, is used :

3 c.c. of the oil, 3 c.c. of carbon disulphide and 1 c.c. of concentrated sulphuric acid are shaken together for some minutes : the mixture should become brown.

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**Pharmaceutical castor oil,** according to the official Italian pharmacopœia, should be obtained by pressure in the cold from husked, peeled seeds ; it should be almost colourless or yellowish, and not of acrid taste, soluble in 5 parts of alcohol at 15° and in 2 parts at 25° and extremely soluble in absolute

TABLE XLIV  
Characters of Vegetable Oils<sup>1</sup>

Fatty	Specific Gravity at 15°.	Solidifying Point.	Zeiss Butyro-refractometer Reading.		Maumené Number (J = Jean, T = Tortelli apparatus).	Saponification Number.	Iodine Number.	Fixed Acid Number.	Volatile Acid Number.	Melting Point.	Solidifying Point.
			t.								
• • • • •	0.914-0.920	-10 to -15°	25°	64-65	50-51 T	187-196 (192)	93-103 (95)	96-97	—	12-15°	5-11°
el • • • • •	0.915-0.921	-14 to -20	25	65-67	60-61 T	187-193	96-109 (100)	95-96	—	2-7	0-4
• • • • •	0.916-0.920	-3 to -7	25	62-67	51-60 T	185-197 (193)	83-103 (92-95)	95-96	1	27-33	22-32
s (Andansonia) •	0.915-0.919	+3 to -3	—	—	—	190-192	76-79	—	—	35-38	32-34
• • • • •	0.920-0.922	-17	—	—	63-65 J	191-196	104-111	95	—	23-24	17
• • • • •	0.912-0.919	0	?	50-60	—	185-188	72-112 (80-84)	95	0.5	—	37-38
rigosperma Gaertn.) •	0.917-0.919	0 to -4	—	—	50-52 J	170-194	90-106	—	—	28-30	25-27
exelsa H.B.) •	0.920-0.933	-18	—	—	103 T	188	132-153 (150)	—	—	18-20	13-14
erman sesamé oil) •	0.920-0.926	-18 to -20	?	76	—	179-195	136-164	90	1-3	18-21	13-15
Kekuna) • • • • •	0.916	—	25	62	—	179-195	60-84	—	—	—	—
bluccana, A. triloba • • • • •	0.960-0.973	-10 to -18	25	78	74 T	176-186 (180)	82-91 (85)	—	2-3	13	2-3
vision • • • • •	0.913-0.918	-3 to -10	25	68-71	61-62 T	167-180 (177)	94-106 (100)	95-96	0.5	17-24	12-18

live	0.923-0.933	25	64-68	95 J	189-195	73-90	3-4	27-30
live	0.925	—	—	—	182	92	—	32-35
live	0.930-0.937	25	81-87	124-138 T	187-195	164-194	—	17-24
live	0.926-0.935	—	—	96-101 J	192-193	(170-190)	—	13-20
live	0.921-0.926	25	71-72	82 T	188-198	117-120	—	20-22
live	0.918-0.919	—	—	—	(190)	111-128	0.3-4	14-16
live	0.915-0.920	25	69	74-77 T	174-182	94-96	1-2	—
live	0.917	—	—	—	174	96-122	—	15
live	0.916-0.920	40	60	—	172-180	105	—	—
live	0.913-0.920	40	85-86	58-59 T	170-176	102-108	0.3-1	12-14
live	0.923-0.928	40	63	91-96 T	189-192	92-103	—	28-30
live	0.913-0.919	25	62-63	41-47 T	185-196	126-134	0.5	21-24
live	0.916-0.918	—	—	(44)	(192-195)	79-88	0.3	—
live	0.918-0.923	25	63-67	51-53 T	189-192	94-96	—	4-7
live	0.930	—	—	—	189-190	206	—	—
live	0.918	25	62	55 T	191-192	86-93	—	13-14
live	0.912-0.919	25	63-64	44-45 T	189-192	91-101	—	17-20
live	0.924-0.937	25	71-74	88-89 T	190-198	131-157	—	7-15
live	0.914-0.918	40	57-58	51-52 J	(193)	93-112	0	15-17
live	0.907-0.923	25	68-69	67 T	173-179	96	0.3	13-15
live	0.922-0.930	—	—	—	181-198	91-108	1	28-29
live	0.928-0.938	25	77-78	101-120 T	191-206	117-141	0.3	15
live	0.922-0.926	25	66-70	—	186-195	126-150	1-2	7-12
live	0.924-0.929	25	73-74	71 T	187-193	(140)	1	23-32
live	0.939-0.943	25	86	83 T	(190-192)	102-116	—	(23-30)
live	0.923-0.936	25	72-73	136-138	182-193	115-137	0.1	16-25
live	0.920-0.924	25	71-72	88 T	(185)	(133-135)	—	20-29
live	0.925-0.926	40	65-68	—	204-210	145-161	1	(20-21)
live	0.924-0.929	—	—	—	188-194	120-137	—	12-13
live	0.924-0.929	—	—	—	183-191	(133)	—	17-18
live	0.924-0.929	—	—	—	188-197	106-118	2	—
live	0.924-0.929	—	—	—	(194)	143-152	0	13-16
live	0.924-0.929	—	—	—	182-190	(148)	—	29-30
live	0.924-0.929	—	—	—	—	115-123	—	30-40

1 The numbers in brackets indicate the more common limits or mean values.

*Castor oil for industrial purposes* (soap-making) may have impurities up to 1%; D = 0.960–0.974; iodine number, 8; melting point,  $-10^{\circ}$  to  $-18^{\circ}$ ; solidifying point of the fatty acids = 3; melting point of the fatty acids = 153.4–156; Maumené number (Tortelli

## SESAMÉ OIL

From the seeds of *Sesamum indicum* and *S. orientale* deep yellow, of faint special odour and pleasant taste. 2 grams dissolve in 1000 c.c. of absolute alcohol at  $15^{\circ}$ . Iodine value given in Table XLIV.

With Heydenreich's, Hauchecorne's, Brullé's and Belloc's gives the colorations usual for seed oils. Characteristic is the following colour reaction, which serves to detect it in all other oils and fats.

**1. Villavecchia and Fabris Reaction.**<sup>1</sup>—Two or three drops of a 1% alcoholic furfural solution (2 grams of furfural in 100 c.c. of alcohol) and then 5–10 c.c. of the oil and 10 c.c. of pure conc. HCl (D 1.19) are poured into a test-tube, the whole being well shaken for a few moments and then left to stand. The acid, coloured dark red, remains in the lower part of the tube and becomes increasingly dark on standing. The oily layer represents a yellowish-red emulsion. The coloration is observable even with mixtures containing only 0.5% of oil.

No other oil gives such a reaction; only certain olive oils (from Algeria, and some from Bari, Brindisi and Lecce) may yield with the reagent a pink or reddish colour, which is, however, always quite different in tint from that produced by sesamé oil. The reaction may be carried out with the liquid fatty acids separated by the method of Ruggeri's method (see General Methods, 18, 1).

**2. Detection of Adulterations.**—Sesamé oil may be distinguished from drying oils, colza oil and arachis oil: the first raise the iodine value, the Maumené number, while the others are detectable by the presence of arachidic and lignoceric acids and by the Tortelli and Belloc's tests (Arachis Oil and Colza Oil).

\* \* \*

*Comestible sesamé oil* should be clear, of normal taste and not too acid (fresh oil may contain 0.5–5% of free acids, calculated on the oil; old oils may contain as much as 35%).

The permissible limits for the *industrial oil* (for soap-making)

<sup>1</sup> This reaction (see *Zeitschr. für angew. Chemie*, 1892, p. 509, and

é number (Tortelli) =  $71.3^{\circ}$ ; solidifying point of the fatty acids =  $4^{\circ}$ .

## Vegetable Fats

These are fatty substances of vegetable origin and solid at the ordinary temperature. Among them are also some so-called *Vegetable waxes*, such as carnauba wax and myrtle wax, which are, however, not true waxes but solid since they are composed of glyceryl esters and not esters of higher alcohols.<sup>1</sup> True waxes of vegetable origin include only carnauba wax and others (see Waxes).

The more important vegetable fats are those of cacao, coco-nut, palm oil, almond-kernel, vegetable tallow and a few others which are described; their characters are given in Table XLV, together with those of other vegetable fats of some interest.

### CACAO BUTTER

#### (Cocoa Butter)

Cocoa butter, from the seeds of *Theobroma cacao*, is a somewhat brittle, yellowish-white solid with a taste and smell recalling those of torrefied cacao. It dissolves in 5 parts of boiling absolute alcohol and is almost insoluble in cold alcohol; it is soluble in 3 parts of ether. It does not readily turn rancid, and only when very old or badly stored does it contain more than 0.5% free acid (calculated as oleic acid); the rancid fat is white. Fat from the skins of cacao seeds is, however, markedly acid even when fresh. The characters of the fat are given in Table XLV.

**Detection of Adulterations.**—It may be adulterated with coco-nut oil, vegetable tallow, stearine, solid paraffin and wax, or, more rarely, with other vegetable fats (Japan wax, Dika oil), almond oil, hazelnut oil or other seed oils. Such adulterations are detected by determining the different characters of the fat, bearing in mind the following:

Coco-nut oil raises the saponification number and the volatile acid number, but lowers the iodine number and the refractometric reading. Almond oil raises the acid number and lowers the iodine number, and is, more readily detectable by its ready solubility in alcohol. Solid paraffin lowers the saponification number and the iodine number and may be recognised in the unsaponifiable portion. Vegetable oils in general lower the specific gravity and the melting point and raise the iodine number and the refractometric reading. Japan wax increases the density, the acid number and the saponification number and lowers the iodine number. Dika

TABLE XLV  
Characters of Vegetable Fats <sup>1</sup>

	Specific Gravity. t.	Melting Point.	Solidifying Point.	Zeiss Butyro- refractometer Reading. t.	Saponi- fication Number.	Iodine Number.	Fixed Acid Number.	Volatile Acid Number.	Fatty Acids.		
									Melting Point.	Solidifying Point.	Acetyl Number.
ang fat) pus	100°	34-43°	22-27°	40°	191-196	29-30	95-96	—	54-55°	48-54°	—
. .	15 100	26-36 (30-35)	20-27	40	192-204 (195)	28-42 (35-40)	94-95	1-4	48-53	45-51	3
oulou- et)	15	23-31	18-26	—	195-196	65-72	93-94	4-5	36	32-33	—
diroba bl.) <sup>2</sup>	—	liquid	—	—	—	—	—	—	—	36	—
. .	40	15-20	8-10	—	198-202	72-84	—	3-4	—	35-39	—
. .	15 100	20-28	14-26	40	246-268 (260)	8-10	83-92	7-9	21-27	16-20	—
ba oil)	15 100	30-42	27-35	—	244-245	5	—	0.4	—	3-5	—

board.	100	0.857	35-45	25-37	—	—	198-221	40-47	93	1-4	51-55	44-52	—
allow)	15	0.917	25-42	20-36	40	52	190-200	60-68	94-95	1-2	39-45	38-41	—
.)	100	0.897-0.898											
.	15	0.995-1.000	40-48	39-45	40	55	205-217	10-11	—	—	47-48	46	—
.	100	0.875-0.878											
ter)	40	0.898	44-47	38-40	40	52	182-190	56-59	94-96	1-3	46-51	43-47	13
ter).	15	0.945-0.996	25-51	24-44	40	48-85	154-191	31-81	—	1-4	40-49	39-45	—
ult)	100	0.884-0.898	(25-30)										
.	15	0.945-0.947	30-43	26-40	40	47	195-207	34-58	95-98	1	44-50	40-49	18
.	100	0.858-0.860											
.	15	0.952-0.955	23-30	20-27	40	36-37	241-260	10-20	87-92	4-7	20-28	20-25	2-9
.	100	0.867-0.873											
Karité													
.	15	0.953-0.955	23-31	17-27	—	—	177-187	49-67	94-95	1-2	39-56	38-54	—
.	100	0.859-0.896											
stable]													
.	—	—	47-52	45-50	50	38	205-231	16-19	—	—	55-57	53-54	—
vege-	15	0.918-0.922	36-47	27-34	40	44-45	196-207	28-100	95-96	1	53-57	52-55	—
.)	100	0.860						(30-45)					
.	20	0.912	39-43	32-33	—	—	219-220	9-10	93-94	—	42-46	—	—
Piney)	15	0.915	36-42	30-40	40	42-47	188-192	30-45	95	0.3	56-57	54-55	—
.	100	0.890											
.	50	0.896-0.900	41-47	38-45	—	—	221-244	12-14	—	—	38-43	36-30	—

n brackets indicate the more usual limits or mean values.

<sup>a</sup> Dextro-rotatory.

<sup>b</sup> Dextro-rotatory:  $[\alpha]_D = 52-57^\circ$ .

<sup>c</sup> Dextro-rotatory:  $[\alpha]_D$  about



and in glacial acetic acid and of glycerol in a mixture of alcohol and ether, as suggested by Grignard.

\* \*

Cacao butter is to be regarded as genuine when its physical characters lie within the limits indicated in Table XLV and it is free from any of the above-mentioned impurities.

It should be noted that *substitutes for cacao butter* are so numerous, e.g., *chocolate butter*, consisting of coco-nut oil ; *cacao butter* (oil and Japan wax). The so-called *Samana cacao butter* is a solid at about  $12^{\circ}$  and when left for a long time separates a liquid at  $17.5^{\circ} = 0.906$ , refractometric reading at  $40^{\circ} = 50.5$  and  $n_D^{20} = 53.59$ .

## COCO-NUT OIL

From the albumin or pulp of the coco-nut, fruit of *Cocos nucifera*, white or pale yellow, and has the consistency of butter and a faint odour. In coco-nut butter well refined for comestible use this odour is lacking, but boiling with a little alcohol and a few drops of acetic acid brings out the odour distinctly.

It dissolves in 2 vols. of absolute alcohol at  $30^{\circ}$  and in 90% alcohol at  $60^{\circ}$ . Its physical and chemical characters are given in Table XLV.

With Heydenreich's, Hauchecorne's or Brullé's reagent it gives a sensible coloration, and it does not react with silver nitrate solution and hydrochloric acid. Characteristic of coco-nut oil are its high saponification number, the low iodine number and the volatility, which is greater than those of vegetable oils and fats in general.

\* \*

*Pure, edible coco-nut oil* is perfectly white (sometimes described as imitate butter), odourless and neutral or almost so (acidity number = 1% as oleic acid) and has a fresh, pleasant taste.

*Industrial coco-nut oil* (for soap) is white or faintly yellow and has more or less pronounced taste and smell. The finest and whitest is known as *Cochin neige*, while the others are called *White Cochin*, *Yellow Cochin*, *oils*.

The allowable limits for these industrial oils are : acidity number up to 4% for Cochin and up to 10% for other qualities ; moisture up to 1% ; impurities, up to 1% ; m.pt. =  $20-28^{\circ}$ , setting point =  $22-1^{\circ}$  (melting point of the fatty acids) =  $16-23^{\circ}$  ; volatile acid number = 10-15 ; saponification number = 248-260 ; iodine number = 7.68-9.5.

## PALM OIL

esterol (see General Methods, 19).  
 value depends essentially on the content of moisture and foreign  
 acids and on the setting point of the fatty acids (titer). These, then,  
 are the principal determinations made (see General Methods, 1, and also  
 2); the acid saponification number is also measured and sometimes  
 the free fatty acid content (see General Methods).

\* \*

The titer of palm oil generally lies between  $40^{\circ}$  and  $50^{\circ}$ . Its content of  
 moisture and foreign matters varies from 0.5% to 17%, but with a good specimen  
 it does not exceed 2%. Commercial palm oil is always markedly acid; when  
 freshly prepared the oil may contain about 10% of free acids (calculated as  
 stearic acid), but most commercial oils show 20–50%, while certain old oils  
 of the same type may contain nearly 90%. As a rule the content of glycerine  
 increases as the free acid increases.

The best commercial oil is that from *Lagos*, with 2% of moisture and im-  
 purities at most; minimum titer,  $43^{\circ}$ ; acidity usually not greater than 20%;  
 saponification number, 196–207. The *Benin* oil, which is brown, has the titer  
 and acidity up to 50%.

## PALM-KERNEL OIL

From the seeds of the oil-palm (*Elaeis guineensis* and *E. melanococca*),  
 the consistency of butter, is white or yellowish, has a special odour  
 different from that of coco-nut oil and readily becomes rancid. In all its prop-  
 erties it closely resembles coco-nut oil (see Table XLV), from which it is  
 difficult to distinguish it. Analysis of this oil is carried out like that of  
 coco-nut oil (*q.v.*).

\* \*

Palm-kernel oil for industrial purposes up to 1% of moisture and ex-  
 cessive impurities are allowed and up to 10% of free acids; saponification  
 number = 241–250; volatile acid number = 4.8–5.6; titer =  $20.5$ – $25.5^{\circ}$ .

## OTHER VEGETABLE FATS

Among the other vegetable fats the following are commonly known and used:  
**Vegetable Tallow or Chinese Tallow** (*Stillingia fat*), from the seeds of  
*Stillingia sebifera*. Its characters and properties may vary with the  
 method of extraction, but it is usually solid, hard and white outside and  
 more or less stained with earthy and vegetable residues, yellowish inside,  
 odourless, or almost so.

**Pé-nut Butter, Fat or Oil** (*Mahwa fat*), from the seeds of *Bassia*  
*latifolia*. It is a soft, yellowish or greenish colour and

## Animal Fats

The most important animal fats are : butter, dealt with on milk and its products (see Vol. II, Chapter II), tallow and the foot-oils, which are considered below in detail ; of other fats are obtained from different animals, but few are. The characters of these are given in Table XLVII.

So-called *wool fat*, which from its composition is to be wax, is dealt with in the article on waxes.

## TALLOW

This is a fat obtained from bovine (ox-tallow) and from (sheep's or goat's fat). It is stiff and yellowish and has a smell ; in the light and air it rapidly becomes rancid and does. part of it dissolves in 40 parts of 94% alcohol. Its physical characters are given in Table XLVII.

Its analysis includes firstly the determination of the melting point of the fatty acids), on which depends the commercial value. Determinations are also to be made of the water and for the of the acid and saponification numbers and, sometimes, of (see General Methods). Any adulteration with bone fat, wax or coco-nut oil, may be detected as described below (2).

**1. Titer Test.**—The sample for this determination is carefully, portions being taken from each cake or cask (at least of the bulk and these melted together at a temperature not above and the fused mass continually stirred until it reaches the melting perature.

50 grams of this sample are saponified with 40 c.c. of 10% solution (D 1.4) and 40 c.c. of 96% alcohol. The soap is dissolved in a litre of water and boiled in a dish to expel the alcohol, the fat is then separated by means of a slight excess of dilute sulphuric acid, boiling continued until these acids form a perfectly limpid liquid, suspended clots. The aqueous liquid is siphoned off and the residue washed with hot water until they no longer give an acid reaction with litmus and then solidified by cooling. The disc of solid acids is washed in a water-bath, filtered through a dry filter in a boiling water-bath, filtrate left overnight in a desiccator.

The setting point of the fatty acids thus obtained is

...tube and in the mass of the liquid. When  
 ...crystals appear throughout the liquid, the  
 ...is stirred gently with the thermometer until it  
 ...becomes pasty and opalescent and prevents the bulb  
 ...of the thermometer from being seen (stirring for 12-  
 ...seconds usually suffices); it is then left at rest.

...before and during the stirring the column of the  
 ...thermometer is carefully observed. It falls at first  
 ...and regularly, but at a certain point the fall  
 ...stops, then stops, and towards the end of the  
 ...operation gives way to a rise to a maximum, the  
 ...persisting for about two minutes. This station-  
 ...temperature represents the solidifying point (titer)  
 ...of the fatty acids examined.<sup>1</sup>

...The result is controlled by re melting—after some  
 ... (preferably 12 hours)—the fatty acids at a tem-  
 ...perature not more than 5° above the solidifying point  
 ...and allowing the molten mass to solidify in the  
 ...conditions as before.

...When the titer of a tallow is known, its yields of  
 ...acids (oleic) and solid acids (stearic and pal-  
 ...may be deduced from *Dalican's Table* (XLVI), which has been  
 ...compiled empirically by mixing a typical commercial stearine with  
 ...solidifying point 54.4° with oleic acid freed from solid acids by pro-  
 ...long standing and filtration. It indicates the percentages of stearic  
 ...and oleic acids in a tallow, a deduction of 4% having been made for the  
 ...moisture and impurities.

...The percentage of stearic or oleic acid in a mixture of fatty acids is  
 ...found by the formula

$$\frac{a \times 100}{95},$$

...where *a* is the percentage of stearic or oleic acid given in *Dalican's table*.

**Detection of Adulterations.**—(a) Bone and wool fats: by the  
 ...method. They lower the saponification number (especially wool fat) and  
 ...if unsaponifiable matter is extracted, this contains a considerable amount  
 ...of cholesterol (*see General Methods*, 19).

(b) Palm oil and coco-nut oil; by the odour; they raise the saponifi-  
 ...cation number, and the latter oil lowers the iodine number.

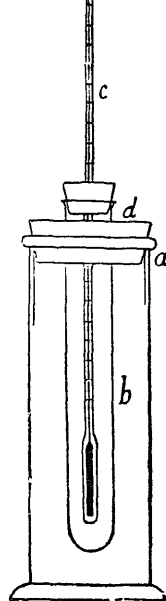


FIG. 58

In place of the arrangement indicated above, Shukoff uses a vacuum-jacketed  
 ...into which 30-40 grams of the fused acid are poured. The vessel is then

TABLE XLVI

Solidification Point.	Stearic Acid %	Oleic Acid %	Solidification Point.	Stearic Acid %
35°	25.20	69.80	44.5°	49.40
35.5	26.40	68.60	45	51.30
36	27.30	67.70	45.5	52.25
36.5	28.75	66.25	46	53.20
37	29.80	65.20	46.5	55.10
37.5	30.60	64.40	47	57.95
38	31.25	63.75	47.5	58.90
38.5	32.15	62.85	48	61.75
39	33.45	61.55	48.5	66.50
39.5	34.20	60.80	49	71.25
40	35.15	59.85	49.5	72.20
40.5	36.10	58.90	50	75.05
41	38.00	57.00	50.5	77.10
41.5	38.95	56.05	51	79.50
42	39.90	55.10	51.5	81.90
42.5	42.75	52.25	52	84.00
43	43.70	51.30	52.5	88.30
43.5	44.65	50.35	53	92.10
44	47.50	47.50		

(c) Other vegetable oils: by the increase in the iodine colour reactions, and by testing for phytosterol (*see* Hog's

(d) Cottonseed stearine: by Halphen's reagent (*see* Co

(e) Mineral substances (gypsum, talc and the like): portion insoluble in ether.

\* \* \*

Pure tallows of good quality give about 95% of fatty acids at 44°, the commercial valuation being made with 43.5° as basis. The acid value is 195-200. They give a mean of about 9.5%.

According to the Union of Italian Soap-makers, the titer of acid should not be below 43.5°, while that of mutton-tallow may vary from 40 to 45°. In different varieties the acidity allowed varies from 3% to 5% and impurities allowed up to 1%.

## OLEOMARGARINE

This is the semi-fluid part expressed from tallow at about

Specific gravity at 15° . . . . .	0.924-0.930
"    "    "    98-100° . . . . .	0.859-0.863
Melting point . . . . .	32-35° (sometimes up to 40°)
"    "    of fatty acids . . . . .	40-43°
Solidifying point of fatty acids. . . . .	39-42°
Weiss refractometric reading, at 35° . . . . .	50-52°
"    "    "    "    40° . . . . .	47-49°
Acid number, if fresh and well stored . . . . .	0
Saponification number . . . . .	192-200 (195-198)
Iodine number. . . . .	42-55 (43-48)
Fixed acid number . . . . .	95-96
Volatile "    "    . . . . .	0.4-1.0

Under the polarising microscope it behaves like fused butter (*see* 3 in article Butter, Vol. II, Chapter II).

## HOG'S FAT

Hog's fat is, strictly speaking, the fat of the inside of the animal, that is, the fat of the inside of the skin constituting *lard*.

American hog's fat is divided into various qualities according to the method of preparation.

Generally the fat is white and pasty, with a peculiar odour and a sweetish taste; it becomes rancid easily, turning yellow. It is only slightly soluble in alcohol. With the ordinary reagents for oils it gives no colour reactions. The characters are given in Table XLVII.

**Detection of Adulterations.**—Lard is adulterated with or even replaced by mixtures of tallow, pressed tallow (also hardened or hydrogenised oils), lard, lardseed stearine or other vegetable fats, or cottonseed, sesamé, arachis, rapeseed, sunflower-seed, coco-nut or lard oil; also with pressed lard and vegetable oils. The artificial mixtures constituting *lard substitutes* often contain a small proportion of lard, recognisable mainly by its characteristic taste. Lards containing marked amounts of water, incorporated with emulsifier, help of a little alkali, are also found.

The various adulterations are detected as follows:

**WATER, ALKALI AND OTHER MINERAL SUBSTANCES.** The water is determined by drying the fat at 100° to constant weight. Alkalis and mineral matters may be found by incinerating the fat and examining the ash; the former may also be detected by treating with hot water and litmus paper, or by passing a current of steam for half an hour through a mixture of 60 grams of the fat with 60 grams of water, then allowing the mixture to cool and filtering: in presence of an alkali or an alkaline earth.

(a) *Preparation of the glycerides.* In a beaker of about 150 c.c. 50 grams of the fused and filtered fat are dissolved in 50 c.c. of ether, the beaker being covered with a clock-glass, cooled to  $15^{\circ}$  and then, by shaking, allowed to crystallise. After an hour the mass is poured into a funnel containing a perforated disc covered with a layer of filter pulp, the liquid being pumped off and the crystalline mass is then pressed with a watch-glass to free it from mother-liquor. The residue is then dissolved again in 50 c.c. of ether and after an hour filtered.

The melting point of the glycerides thus obtained is  $55-60^{\circ}$  for pure lard, but lower if tallow is present. If the melting point is below  $61^{\circ}$ , the glycerides must be recrystallised from ether in the same manner until a portion melting at least as high as  $61^{\circ}$  is obtained. For the certainty, it is necessary that the glycerides melt between  $60^{\circ}$  and  $65^{\circ}$ .

To obtain a good crystallisation of the solid glycerides from soft fats rich in liquid glycerides, the ethereal solution is cooled to  $5-10^{\circ}$ , or use made either of a mixture of 3-4 parts of ether with 1 of alcohol, or of anhydrous acetone.

(b) *Preparation of the fatty acids.* From 0.1 to 0.2 gram of pure lard, m.p.  $61-65^{\circ}$ , is finely subdivided and placed in a beaker with 100 c.c. of a seminormal colourless alcoholic solution of potassium permanganate. The liquid is boiled carefully for 5-10 minutes to bring about complete oxidation, the soap being dissolved in 100 c.c. of water and the solution transferred to a separating funnel, decomposed with 2-3 c.c. of 25% sodium hydroxide acid and extracted with 25 c.c. of ether. The filtered ether is evaporated and the residue dried at about  $100^{\circ}$  for 30-60 minutes, cooled, finely powdered.

(c) *Determination of the melting points.* The melting points of the glycerides and of the fatty acids prepared according to (a) and (b) are determined under identical conditions. For this purpose two perfectly similar U-tubes are used. With the help of a pipette a finely powdered substance is introduced into one of the limbs of the U-tube so as to form a layer 2-3 mm. deep. The two tubes are then joined by a thermometer so that the branches containing the substance are at the bulb and the whole heated in a water-bath; when a temperature of  $50^{\circ}$  is reached, the heating is adjusted so that the rise in temperature is only  $1.5-2^{\circ}$  per minute. The temperature at which the substance becomes liquid, clear and transparent is taken as the melting point. The determination should be repeated with fresh substance and the concordant results taken.

With pure hog's fat the difference (d) between the melting points of the glycerides (M.G.) and of the fatty acids (M.A.) is about

	M.G.		<i>d</i>	M.G.	<i>d</i>
0°	5.00°	62.5°	4.25°	64.0°	3.50°
5	4.75	63.0	4.00	64.5	3.25
0	4.50	63.5	3.75	65.0	3.00

For each 0.1° variation in M.G. the difference *d* changes by 0.05°, and minimum M.G. + 2*d* is never less than 71 with pure hog's fat. Hog's fat containing tallow of whatever origin or pressed tallow or hardened oil has a lower value of *d* than is shown in the above table, while M.G. + 2*d* is less than 71.

EXAMPLES: A hog's fat gave: M.G. = 63.5° and M.A. = 58°, so that 58 + 2*d* = 71 and M.G. + 2*d* = 74.5°; the fat is thus pure. Another fat gave: M.G. = 63° and M.A. = 60.5°, so that *d* = 2.5° and M.G. + 2*d* = 68. This fat contains tallow (pressed tallow, hardened oil).

VEGETABLE OILS AND FATS. COTTONSEED STEARINE. These adulterations are detected as follows:

*Colour reactions.* Bellier's reaction (*see* General Methods, 23, 4) for the presence of seed oils in general; Villavecchia and Fabris' reaction for sesame oil (*q.v.*); Halphen's reaction and the silver nitrate reaction for cottonseed oil (Armani or Tortelli and Ruggeri, that of cottonseed stearine (Cottonseed Oil)).

Arachis oil is detected by the reaction for arachidic and lignoceric acids (Arachis Oil).

*Various characters.* Determinations are also made of the saponification number, volatile acid and Polenske numbers (*see* General Methods, 8 and 9, this chapter, and Butter, Vol. II), which detect the presence of coconut oil; of the ordinary and absolute iodine numbers (*see* General Methods, 11 and 13), which serve to confirm the presence of seed oils and to give an approximate indication of their quantity (when the nature of the vegetable oil has been ascertained); and of the rotatory power, for the detection of castor oil (Carpinus (Maratti) and Mowrah fats (*see* later, d)).

In addition to these subsidiary determinations, measurements may also be made of the refractive index (Refractometric reading at 40° (*see* Butter) and of the Maumené number (General Methods, 21).

*Detection of phytosterol.* This is of special importance in the analysis of vegetable oils, since only with its help can it be decided if vegetable oils have really been pure.

Like all other animal fats and oils, hog's fat contains, as unsaponifiable matter, cholesterol (about 0.2% in the crude state) whereas the un-



The united alcoholic liquids, which contain the unsaponifiables, are boiled with 15 c.c. of 30% sodium hydroxide solution until saponification is complete, the liquid being evaporated almost to dryness and the residue extracted with ether. The ethereal solution is evaporated and the residue left taken up in a little ether, filtered and the ether evaporated. The final residue is dissolved in a little boiling absolute alcohol containing a few drops of dilute acetic acid and crystallised.

Repetition of the crystallisation from a little boiling absolute alcohol yields the *sterols* (cholesterol and phytosterol) ready for microchemical examination. With practice and by comparisons of mixtures of known composition, the crystalline form observed under the microscope indicates whether the cholesterol is pure or mixed with phytosterol; the character of the latter is evident in mixtures containing only 5% of cholesterol. (Figures given under General Methods, 19).

The acetyl compound is then prepared as follows: The residue left together with the last mother-liquor, are freed from alcohol by evaporation in a glass dish on a water-bath, the residue being boiled for 5 minutes with 3-5 c.c. of acetic anhydride, the dish being covered with a glass cover while; the cover is then removed and the solution evaporated to dryness on a water-bath. The residue is dissolved in boiling absolute alcohol (20 c.c.) and the solution left to crystallise at the ordinary temperature. When about two-thirds of the alcohol have evaporated, the crystals are collected in a small filter and washed with 2-3 c.c. of 95% alcohol, being then dried by pressing between filter-paper and dried in a vacuum desiccator. The residue is dissolved in 5-10 c.c. of boiling absolute alcohol and left to crystallise. The operation is repeated three times. After the third crystallisation the melting point of the crystals is determined, two further crystallisations followed by determinations of the melting point being carried out.

(2) *Digitonin method*<sup>2</sup>: 50 grams of the fat are dissolved in 120 c.c. of chloroform and the liquid heated on the water-bath at 60° with 20 c.c. of a 1% solution of digitonin in 96% alcohol, with shaking; it is then left at rest overnight. The cholesterol and other sterols combine with the digitonin forming insoluble products (*digitonides*) which are deposited at the bottom of the chloroform solution. The supernatant liquid is filtered and the precipitate washed on the filter with 96% alcohol and dried in the air.

<sup>1</sup> *Zeitschr. für öffentl. Chem.*, 1897, p. 10.

<sup>2</sup> This method may be applied under the conditions laid down by Schilling (*Chem. Zeit.*, 1913, p. 1001) or by Klostermann, Fritzsche and Opitz (*Zeitschr. Unt. Nahr. Genussmittel*, 1913, XXVI, pp. 1-10, XXVII, p. 512). The method now described is deduced from the

acetyl-compound thus obtained determined after the second, third or fourth crystallisation.

*Melting point of the acetyl-compound.* This is determined in a very thick glass U-tube, into one branch of which the powdered substance is introduced to form a layer 2-3 mm. deep. The observed melting point is then corrected by means of the formula,

$$x = T + [n(T - t) \times 0.000154],$$

where  $x$  = correct melting point,

$T$  = observed melting point,

$n$  = length of mercury column of thermometer protruding from the tube, expressed in degrees,<sup>1</sup>

$t$  = mean temperature of the air about the protruding part of the thermometer, determined with another thermometer placed near the first with its bulb at the middle of the protruding portion of the stem.<sup>2</sup>

The corrected melting point of cholesterol acetate is  $114.3-114.8^\circ$ , whilst that of phytosterol acetate is above  $125^\circ$ .

d) *Rotatory power.* This is determined on the fat as such or on the unsaponifiable substances extracted from it. In the former case, which is preferred for the detection of Hydnocarpus oil, the rotatory power of the fat is determined in benzene solution at a temperature of about  $20^\circ$  with an ordinary shadow polarimeter. From the observed rotation the specific rotation  $[\alpha]_D^{20}$  is calculated by means of the formula,

$$[\alpha]_D^{20} = \frac{100\alpha}{lc}$$

where  $\alpha$  is the observed angle in circular degrees,  $l$  the length in decimetres of the tube used, and  $c$  the concentration, i.e., the number of grams of substance in 100 c.c. of the solution.

The determination of the rotatory power of the unsaponifiable substance is effected in the manner indicated by Berg and Angerhausen for the detection of Mowrah butter in lard.<sup>3</sup>

\* \* \*

Genuine hog's fat should not contain appreciable quantities of water, alkaline substances or other mineral matters, and should be free from all extraneous matters and oils.

Its physical and chemical characters should lie within the limits given in Table XLVII. A saponification number above 200, volatile acid and Polenske numbers higher than 1, and an iodine number below 45 demonstrate the presence

<sup>1</sup> For instance, if the thermometer is immersed up to  $+5^\circ$  and the observed melting

cottonseed, sesame or other seed cake. In such cases, addition of the lard is proved only when the presence of phytosterol is the case when the acetyl-compound of the sterols obtained has a corrected melting point higher than  $115^{\circ}$ .

Lard which gives the colour reactions but does not contain phytosterol cannot be regarded as containing vegetable oil.

The melting point difference, determined by Bömer's method, must be such that the value of  $M.G. + 2d$  is 71 or more; if this value is less, the lard is considered adulterated with tallow, pressed tallow, or both.

In general, the following conclusions, based on the melting point difference and the phytosterol test, may be drawn<sup>1</sup>:

I. The melting point difference is normal: the lard is either pure or adulterated with vegetable oils. The phytosterol test (m.pt. of acetyl-compound of the sterols) will demonstrate the presence or absence of vegetable oils.

II. The melting point difference is below the normal ( $M.G. + 2d < 71$ ): the following cases present themselves:—

1. Phytosterol test negative: lard contains tallow, hardened oils, or both.

2. Phytosterol test positive: there may be—

(a) Addition of vegetable oils or hardened oils;

(b) „ of tallow (or pressed tallow) and vegetable oils;

(c) „ „ „ „ „ hardened oils.

## BONE FAT

This is obtained by de-fatting bones by means of water, benzene, or benzine (benzine, carbon disulphide). It varies in consistency but is granular and granular, and it has a yellowish or brown colour and a peculiar odour. It is somewhat soluble in alcohol, especially when it contains free fatty acid. The physical and chemical characters vary somewhat according to the fat is pure or has been extracted with solvents or steam; see Table XLVII.

Bone fat contains cholesterol and, in accordance with the method of extraction, it may contain various impurities, such as water, gelatinous substances and hydrocarbons.

The analysis of bone fat for the purpose of determining its purity, value, includes the following:

1. **Determination of the Water.**—As indicated in the general method, or more accurately by heating about 10 grams of the fat at  $100^{\circ}$  over a stream of hydrogen to constant weight.

2. **Determination of Extraneous Impurities** (soaps, free fatty acids, and gelatinous substances, etc.).—50 grams of the fat are heated with a quantity of ether sufficient to dissolve the fatty matter, and the

account is to be taken also of the fat combined as lime soap, treatment with ether is preceded by an hour's heating, with occasional shaking, on the water-bath with 3-5 drops of concentrated hydrochloric acid, the lime soaps having been decomposed in this way, the further procedure is as described above.

**Determination of the Ash.**—10 grams of the fat are carefully melted and the residue weighed. The ash of bone fat is composed of calcium oxide and a little carbonate, with small quantities of calcium phosphate, alumina and ferric oxide.

**Titer.**—As with tallow, the titer of bone fat is given by the solidifying value of the free fatty acids, this being determined as in the case of tallow.

**Acid and Saponification Numbers.**—By the general methods, Nos. 7 and 8. The acidity is expressed as percentage of oleic acid.

**Hydroxy-acids.**—As in General Methods, 15.

**Unsaponifiable Substances.**—These may be estimated by saponifying the fat with alcoholic potash and extracting the aqueous solution of the soap with ether (*see* General Methods, 19).

**Recognition of Bone Fat which has been extracted with Benzene.**—According to Gianoli,<sup>1</sup> this may be effected as follows :

a) The fat is subjected to prolonged distillation with concentrated hydrochloric acid solution ; where the fat has been extracted with benzene, the benzene drops which are not soluble in soda float on the surface of the distillate.

b) The fat is saponified with alcoholic sodium hydroxide, the alcohol is removed, the fatty acids liberated and washed with water, and this water is extracted in the hot with ammonia : turbidity indicates the use of benzene.

**Test for American Bone Fat.**<sup>2</sup>—To ascertain if a sample of bone fat of American origin may be used without inconvenience for soap-making, the following test is recommended :

10 grams of the fat and 30 c.c. of water are well shaken in a steam-heated vessel with 20 grams of sulphuric acid (66° Baumé), the mass being afterwards heated and then left to stand : if the fat separates readily and rapidly, it may be regarded as of good quality, but if an emulsion is formed, or if it fails to separate into two distinct forms, the fat will give poor results and a bad yield of soap.

\* \* \*

*Commercial bone fats* may have somewhat varying characters and composition : the water content usually ranges from 1 to 3%, but may reach even 5%. The extraneous impurities vary from 0.5 to 3% and the ash also from 0.5 to 3%. The titer for good products is 36-44°, the acidity may exceed 50%, and the unsaponifiable matters usually lie between 0.5 and 2%.

## FOOT OIL

This is obtained more especially from the feet of the ox and those of the sheep and horse. It is a pale yellow, almost white, solidifying only below  $0^{\circ}$  (at about  $-5^{\circ}$ ). Its characters are given in Table XLVII.

**Detection of Adulterations.**—The oil may be adulterated with vegetable or marine animal oils, these additions being detected by determining the various characters of the oil. Mineral oils are detected by gravity and the saponification and iodine numbers and may also be detected by investigation of the unsaponifiable substances (*see* General Methods). Vegetable oils give Bellier's reaction and the other general reactions of seed oils (*see* General Methods, 23). By means of the special tests, colza, cottonseed and sesamé oils (*q.v.*) may be detected. Foot oil gives no colour reaction and does not contain arachidic acids or erucic acid. The presence of phytosterol would indicate adulteration with vegetable seed oil (*see* Hog's Fat). May be raised to raise the specific gravity and the iodine number and may be used for the special reactions indicated in the article on fish oils,

\* \* \*

For use as lubricants, foot oil should remain liquid and for a long time, should not contain more than 2% of free acids or free fatty acid, and should not contain extraneous oils. A drop lying on a glass plate and kept at  $50^{\circ}$  for 24 hours should not resinify and should be easily removable from the glass.

## Fish and other Marine Animal Oils

These oils may be divided into three classes: (1) *Fish oils* obtained from herrings, sardines, pilchards, sprats, tunny, etc.; (2) *Train oils* from the residues obtained in the preparation of these fish oils (*train oils*), from the marine mammals, the seal and walrus; (3) *Liver oils*, mainly from cod-liver but to a small extent from ray, skate, etc.

Fish and blubber oils and cod-liver oil are treated separately in the following articles; here, however, we shall give certain general tests which are common to the three classes of oil and serve to distinguish them from other fatty substances, either animal or vegetable.

Sp. Fat.	Specific Gravity. t.	Melting Point ° C.	Solidifying Point ° C.	Zeiss butyro- refractometer Reading. t°.	Maumené Number (J = Jean, T = Tortelli apparatus).	Saponi- fication Number.	Iodine Number.	Fixed Acid Number.	Volatile Acid Number.	Melting Point ° C.	Sol. diffy. Point ° C.
• • •	15	—	9	—	—	203-204	80-81	—	—	—	—
• • •	15	20-30	15-25	—	—	170-195 (185-190)	44-75 (50)	86-94	—	30-45	28-42
• • •	—	—	34-35	—	—	—	36-39	—	—	—	—
• • •	—	36-39	22-24	—	—	—	58-59	—	—	—	—
• • •	15	22	8-10	25	47-49 J	184-192	64-82	95	0.4-0.7	34-39	30-35
• • •	100	—	—	—	—	—	—	—	—	—	—
• • •	15	33-40	21-27	—	—	193-194	66-67	—	2	38-40	32-34
• • •	15	25-34	18-22	—	—	191-198	58-71	92-96	1-2	37-41	31-38
• • •	15	36-48	26-32	—	39-40 T	195-200	46-70	95-96	—	35-47	34-40
• • •	100	—	—	—	—	(196)	(60-66)	—	—	—	—
• • •	15	25-39	20-30	—	53-54 T	195-200	78-95	94-97	0.4-2	36-42	30-38
• • •	100	—	—	—	—	—	—	—	—	—	—
• • •	15	—	below 0	—	58-59 T	195-197	73-90	—	—	30-32	28-29
• • •	15	—	—5	40	45-47 T	191-196	69-83 (70-75)	97-98	—	35	31
• • •	100	—	—	—	—	—	35	—	1-2	53-55	48-50
• • •	15	49-52	37-38	—	—	195	64-78	95-96	1-2	28-35	26-27
• • •	15	—	below 0	20	40-41 T	189-200	—	—	—	—	—
• • •	100	—	—	—	—	—	—	—	2	44-46	39-40
• • •	15	37-45	29-38	—	—	195-199	39-55	—	0.5	43-48	38-47
• • •	15	40-49	27-37	40	31-42 T	193-202	36-56 (40)	95-96	—	—	(42-45)
• • •	100	—	below 0	—	—	—	68-75	95	0.7	24-26	21-23
• • •	15	—	32-41	—	41-52 T	194-197	32-46	95-96	—	45-55	40-48
• • •	15	44-52	—	—	—	192-197	—	—	—	—	—
• • •	100	—	0-3	20	—	190-194	113-146	—	0.6	34-37	28-35
• • •	40	—	—	—	—	—	55-57	—	—	—	—
• • •	15	—	—	—	—	—	—	—	—	—	—
• • •	100	—	—	—	—	—	—	—	—	—	—

<sup>1</sup> Numbers in brackets indicate the more common limits and mean values.

liquid is filtered through a steam-heated filter and the precipitate in benzene washed with boiling benzene, dried, and a determination of its melting point, which should be above  $190^{\circ}$  (with position and blackening). If the melting point is below  $190^{\circ}$  it is taken up several times with boiling benzene until a portion at this temperature is obtained.

A reaction similar to the above is given also by the dry walnut and hempseed oils (*see* Linseed Oil); the hexabromides furnished by these oils are, however, soluble in boiling benzene at  $180^{\circ}$  without decomposing.

According to Marcussen, the octabromo-compound test made on the fatty acids and not on the oil as such—is able to distinguish marine animal oil mixed with linseed or other oil.

(b) TORTELLI AND JAFFE'S REACTION. In a graduated cylinder with a ground stopper, 1 c.c. of the oil, 6 c.c. of chloroform, 10 c.c. of glacial acetic acid are shaken together and 40 drops of a 1% solution of bromine in chloroform added; the cylinder is again shaken for a moment and then placed on a white paper and the color observed. Marine animal oils in general give a green color, vegetable oils yellowish or blue reflexion, which increases during the space of 10 minutes and afterwards changes to brown. With vegetable or tallow oils and fats, pale yellow or yellowish colorations are obtained, gradually darkening for an hour and then changing to brown.

For the reaction to succeed, the oil and the reagents must be anhydrous, dehydrated and the vessels very dry. If the oil is highly colored it must be decolorised with sulphuric acid<sup>1</sup> or soda.<sup>2</sup>

## FISH AND BLUBBER OILS

*Fish oils* proper are those obtained from the residues left after the preparation of various fish (sardines, herrings, shad, tunnyfish, etc.). Cetaceans are obtained mainly *Whale oil* and *Seal oil*, dolphin oil and porpoise oil being less common. In general these oils are colorless, but they are turbid and contain more or less abundant solid

<sup>1</sup> 50 c.c. of the oil are treated for 5-6 hours, with occasional shaking, with 10 g. of conc. sulphuric acid and then filtered through a thin layer of filter paper. The filtrate is washed with boiling water to render it free from acid and dried on filter paper in an oven at  $100^{\circ}$ .

<sup>2</sup> 100 c.c. of the oil and 5 c.c. of 30% caustic soda solution are heated in a water bath for a quarter of an hour with frequent shaking, 50-60 c.c. of a 1% ferric chloride solution being then added and the heating on the water-bath continued for three-quarters of an hour, with shaking. The oil is then decanted

With alcoholic potash they mostly give brown soaps ; they contain quantities of unsaponifiable substances (0.5-2%). When dissolved in carbon disulphide and treated with a little conc. sulphuric acid, they give a reddish-brown coloration with no trace of violet (*see* Cod-liver Oil). They give the general reactions for marine animal oils described above and their characters are given later in Table XLVIII. Their analysis includes the following :

**Water, Impurities, Acidity.**—These are determined as in General Methods, 1 and 7.

**Distinction between Fish Oils and Blubber Oils.**—With pure oil of one kind or the other, the iodine and Maumené numbers are sufficient to determine if it is fish oil or whale (or seal) oil (*see* Table XLVIII). A mixture of the two types of oil cannot be identified. The reaction with carbon disulphide and sulphuric acid serves to distinguish fish and blubber oils from liver-oils (*see* following article).

**Detection of Impurities :**

(a) MINERAL AND RESIN OILS. These are detected by saponifying the oil (5-100 c.c.) and extracting and examining the unsaponifiable matter as indicated in General Methods, 19.

(b) VEGETABLE OILS. These are detected by the digitonin test for cholesterol (*see* Hog's Fat). Cottonseed and sesamé oil may also be identified by means of their special colour reactions, provided that the oil is not too much coloured.

## COD-LIVER OIL

This is obtained from the liver of *Gadus morrhua* and of other allied fish of the Northern Atlantic. According to its purity and colour it is divided into *white* (medicinal, superior), which is clear, of pale or straw yellow colour, almost odourless and almost tasteless ; *pale*, which is clear, reddish-brown, and with a marked fishy odour and taste ; *red* or *brown*, which is more or less turbid and brownish-red and with an unpleasant fishy odour and

It dissolves slightly in alcohol, but easily in ether, benzene or other non-aqueous fat solvent. It contains small quantities of unsaponifiable substances (mainly cholesterol) : 0.3-2% in pale oils and up to about 8% in the brown ones.

Further it contains traces of iodine in organic combination (0.002-0.005%). This is not extractable by solvents or by mere saponification, but is detected only by saponifying the oil, adding a little nitre to the soap, and carefully isolating and testing



TABLE XLVIII  
Characters of Marine Animal Oils <sup>1</sup>

	Specific Gravity.	Setting Point.	Zeiss Butyro-refractometer Reading.	Maumené Number (J = Jean, T = Tortelli apparatus).	Saponification Number	Iodine Number.	Fixed Acid Number.	Volatile Acid Number.	Melting Point.	Setting Point.	Acetyl Number.
FISH OILS											
<i>losa menhaden Cuv.</i>	0.927-0.933 (15°)	—	71-72 (40°)	123-128 J	188-193	160-179	—	2-3	—	—	—
<i>pea Harengus</i> . .	0.920-0.939 (15°)	—	—	—	170-194	103-142	95-96	—	30-32	—	—
ardine ( <i>Clupanodon</i>	0.928-0.935 (15°)	—	—	—	189-196	160-190	95-97	—	35-36	—	—
ne . . . . .	0.875-0.878 (100°)	—	—	—	193-200	154-159	—	—	—	—	—
ardine ( <i>Clupea sar-</i>	0.928-0.934 (15°)	20-22°	—	112-113 T	189-196	160-193	94-96	—	30-31	—	21-22
<i>a sprotus</i> . . .	0.927-0.928 (15°)	—	76 (25°)	—	194-195	122-142	95	1-2	28	25-26	8-9
<i>nnus vulgare, T.</i>	0.932-0.933 (15°)	—	89 (20°)	—	185-186	156-199	95-96	—	31	—	22-29
WER-OIL OF											
<i>mon/hua</i> . . . .	0.920-0.938 (15°)	below 0°	75-85 (25°)	102 T	171-193 (185-196)	135-182 (150-170)	95-97	0.2	21-25	13-24	19-51
<i>atus spec.</i> . . .	0.910-0.929 (0.915-0.917) (15°)	—	—	90 J	146-183 (160)	90-138	97-98	1-2	—	—	66
<i>atis, R. Clavata</i> . .	0.931 (15°)	—	—	—	185-186	157	94-95	1	—	—	10-11
MBER OILS											
<i>ena mysticetus, B.</i>	0.916-0.930 (15°)	—	65 (25°)	75-76 T	160-202 (180-190)	90-146	93-95	1-4	14-27	10-24	11-23
the body ( <i>Delphi-</i>	0.872 (100°) 0.918-0.930	—	65-69	—	197-231	99-127	93	11-44	—	—	—

**Acid Number.**—As in General Methods, 7.

**Test for Added Iodine (Inorganic).**—About 10 c.c. of oil are shaken with as much water, the latter being then separated and treated with starch paste and either conc. nitric acid or chlorine water: appearance of a blue coloration indicates inorganic iodine.

**Freezing Point.**—The oil is maintained at  $0^{\circ}$  for some time to ascertain if it remains liquid.

**Detection of Adulterations.**—The oil may contain the following impurities:

(1) **OTHER FISH-LIVER OILS.** No certain methods are known of distinguishing different fish-liver oils or their mixtures.

(2) **FISH AND BLUBBER OILS.** No certain method exists of detecting blubber oil in cod-liver oil. Addition of blubber oil (whale, seal) may be suspected as a result of determinations of the iodine number, the Maumené number and the refractometer reading (Zeiss), which are lowered by whale oil (see Table XLVIII).

(3) **VEGETABLE AND MINERAL OILS.** These are recognised by the methods given in the preceding article (Fish and Blubber Oils).

\* \* \*

According to the Official Italian Pharmacopœia, *medicinal* cod-liver oil is pale yellow or straw-yellow, D at  $15^{\circ} = 0.922-0.930$ , iodine number = 150-170. When cooled to  $0^{\circ}$  it does not congeal, but deposits flocks of white solid matter. It should give the reaction for fish-liver oils and should contain no inorganic iodine (test 3).

The acidity is low in white oils, especially in so-called steam liver oil (0.3% free oleic acid), but is higher (up to 8%) in the more highly coloured yellow oils and may reach about 30% in brown oils.

## Waxes

Waxes are composed essentially of compounds of certain fatty acids (myristic, stearic, cerotic) with higher alcohols (cetyl, myricyl alcohols); they contain also a certain amount of free acids (beeswax, carnauba wax) and solid hydrocarbons (beeswax). Waxes are of animal origin, such as beeswax, Chinese insect wax, wool fat and spermaceti, and of vegetable origin, such as carnauba wax, fig wax, cocuba wax, etc. The latter should not be confused with other vegetable products known as waxes, these being vegetable fats, such as Japan wax and myrtle wax (see Vegetable Fats).

The most important waxes are: beeswax, wool fat, spermaceti

*Crude (virgin)* wax in pale yellow or brown. European yellow or pale yellow, the African and American reddish-yellow and the Indian greyish-brown. It is fatty to the touch and to the heat of the hand, and presents a granular fracture. odour, recalling that of honey, and a faintly balsamic taste.

*White or bleached* wax (decolorised by air and light or by chemicals) is white, brittle, and only slightly fatty and odoriferous.

In general the wax is almost insoluble in cold alcohol but soluble in boiling absolute alcohol, from which it separates on cooling. It is soluble in cold ether, more so in boiling ether, chloroform, and carbon disulphide.

It consists principally of cerotic acid and myricyl palmitate but contains also free melissic acid and ceryl alcohol and other constituents (3-12%, according to the origin).

The physical and chemical characters of different types are given in Table XLIX.

The wax may be adulterated with stearine, colophony, or ceresine, Chinese (insect) wax, carnauba wax, Japan tallow, wool fat, flour or starch, and mineral substances; these may be present. The colour may be enhanced by turmeric or other dyes.

Imitations of the wax are made with paraffin wax, ceresine, or with various mixtures of paraffin wax, carnauba wax, Japan tallow, etc., often coloured with coal-tar colours.

To detect the different adulterations and imitations it is necessary to determine the various characters (*see* 1-5), and to apply certain special tests (*see* 6-13), since it is possible to produce mixtures with the characters of the pure wax. If, on the other hand, the detection of beeswax in mixtures with other substances is required, tests are necessary.

In the case of the crude (virgin) wax, before proceeding with the determination of the characters (1-5), it is well to wash with water to remove the whole of the honey and then to dry the mass in the hot.

**1. Specific Gravity.**—This may be determined most easily by the use of the specific gravity bottle, but Hager's method may also be used. The wax is melted at a gentle heat and poured in drops into cold water, the beads of wax thus obtained being dried in absorbent paper, left overnight to solidify and then immersed in alcohol of known density, e.g., 0.965, at 15°. If the beads remain suspended at a certain depth in the liquid, the specific gravity of the wax is that of the liquid. If, on the other hand, they sink or float, tests are made with more concentrated alcohols until the correct specific gravity is found.

...ed name, the wax being difficultly saponifiable. Exact determinations may be made by Berg's method, modified by Ehrlich and Kurschner: about 4 grams of the wax, 20 c.c. of xylene (recently distilled) and 20 c.c. of absolute alcohol (neutralised) are boiled in a reflux apparatus for 5-10 minutes; titration of the liquid with semi-normal alcoholic potash (with phenolphthalein) gives the acid number. A further quantity of 30 c.c. of the same potash solution is then added, the liquid boiled for an hour, treated with 50-75 c.c. of 96% alcohol (neutral), heated for 5 minutes longer, and the excess of potash titrated with seminormal hydrochloric acid (indicator as above); the ester number is obtained.

In judging a wax (*see later*) it is important to know the acid, saponification and ester numbers, the last being the difference between the first two. The ratio of ester number to acid number, the so-called *ratio value*, is also of importance.

**Iodine Number.**—As in General Methods, 12.

**Refractometric Reading.**—This is determined with the Zeiss refractometer (*see Butter*, Vol. II, Chapter II) at a temperature of 64°. To reduce the reading to the normal temperature of 40°, the difference between 64 and 40, i.e., 24, is multiplied by 0.53 and the product added to the reading at 64°.

**Test for Stearine.**—About 3 grams of the wax and 10 c.c. of 85% alcohol are heated and shaken in a flask until the wax is thoroughly fused and then left to cool for some hours with frequent shaking; only the stearine (and any resin, *see later*, 7) remains in solution. The solution is then filtered and the filtrate diluted with a large amount of water. With the pure wax the liquid remains clear, whereas the presence of stearine (about 1% more) produces a marked turbidity or a white precipitate, which may be collected and identified by means of its melting point (53-55°). The saponification number (about 195), provided of course that Morawski's test indicates that resin is absent.

If resin and other extraneous acid substances soluble in alcohol are present, the stearine (S) added to a wax may be calculated from the acid number found (*a*) by means of the formula:

$$S = \frac{100(a - 20)}{175}.$$

When a wax or a mixture resembling wax contains stearic acid and it is well to eliminate these substances immediately by means of 85% alcohol and to make the other tests and determinations on the insoluble

by means of acetic anhydride (see General Methods, 20).

The quantitative determination may be effected by Tw (see General Methods, 20).

**8. Paraffin Wax and Ceresine.**—As a preliminary test the wax, about 25 c.c. of seminormal alcoholic potassium hydroxide, 20 c.c. of 95% alcohol are boiled for an hour in a reflux apparatus over a naked flame: with pure wax the solution is clear, or almost clear, but so when diluted with hot water, but with wax mixed with ceresine, the liquid remains turbid, and becomes still more turbid with water.<sup>1</sup>

A more certain and even *quantitative* test may be effected by the method<sup>2</sup>: 10 grams of the wax, 25 c.c. of alcoholic potassium hydroxide (KOH per litre of absolute alcohol) and 50 c.c. of pure benzene are boiled for 20 minutes in a reflux apparatus on an asbestos card over a flame, 50 c.c. of water being then added and the boiling continued for 10 minutes. After a short rest, the liquid separates into two layers: a yellowish one (benzene solution of higher alcohols and hydrocarbons) and a lower, somewhat opalescent one (aqueous-alcoholic solution of potassium salts). As soon as the separation is sharp, the lower hot liquid is drawn off with 50 c.c. of hot water, and the liquid boiled for 10 minutes in a reflux apparatus. The aqueous solution is then immediately removed, and the benzenic liquid transferred to a tared capsule, the vessel in which the operations have been conducted being washed with benzene<sup>3</sup>; the solvent is then evaporated on the water-bath, the residue dried at 100° and weighed. This gives the total weight of alcohols and hydrocarbons contained in the wax and from this the combined weight of the various hydrocarbons may be deduced, knowing that in pure wax the percentage of alcohols and hydrocarbons never exceeds 55% (usually 50%).

If desired, the hydrocarbons may, according to Ley, be determined quantitatively from the higher alcohols by means of a mixture of absolute alcohol and conc. hydrochloric acid, in which the latter dissolves (see General Methods, 11); or, as Buchner recommends,<sup>4</sup> the acetyl number (see General Methods, 11) of the mixed higher alcohols and hydrocarbons may be determined and the quantity of the former deduced by taking the difference between the acetyl number of the higher alcohols of the pure wax.

**9. Test for Carnauba Wax and Insect or Chinese Wax.**—No special reactions exist for identifying these waxes in beeswax, but, however, the presence of other extraneous substances has been detected, as any stearic acid and resin eliminated as indicated above (6).

(see later).

**Test for Japan Wax** (from various species of *Rhus*), **Tallow** **other Fats in general**.—A scrap of fused potassium bisulphate is to about 1 gram of the molten wax in a test-tube and the mixture heated over a direct flame: the pure wax gives pungent sulphurous whereas in presence of fats (glycerides) the characteristic irritating of acrolein (due to decomposition of the glycerine) is observed and of filter-paper, soaked in a solution of sodium nitroprusside and piperidine and placed at the mouth of the tube, turns violet-

This test shows the presence of glycerides, the glycerine is determined General Methods, 17: the amount of glycerine, multiplied by 10, gives approximately the quantity of fatty substance in the wax, since fats contain on average about 10% of glycerine.

It should also be borne in mind that Japan wax, tallow and other fats lower the melting point and raise the saponification number (tallow raises the iodine number) of the wax (see later).

**Detection of Wool-Fat and its Products (Wool-Fat Stearine and Wax)**.—The higher alcohols and hydrocarbons are extracted from the wax by Leys' method (8), the mixture thus extracted being tested for sterol by means of chloroform and sulphuric acid (see General Methods, Higher Alcohols).

**Determination of the Water and Various Extraneous Impurities**.—About 5 grams of the wax as it stands are heated at 100–105° to constant weight, the loss representing the water. The residue is dissolved in hot benzene and the solution filtered from any appreciable undissolved portion through a tared filter, the insoluble matter being washed with hot benzene, dried at 100° and weighed. The residue insoluble in benzene is then tested for starchy or mineral matters by the usual methods.

**Extraneous Colouring Matters**.—About a gram of the rasped wax is shaken with ammonia: in presence of *turmeric*, a reddish-brown colouration is obtained.

To detect *coal-tar dyes*, the wax is extracted with 90–95% alcohol in a test-tube. The liquid is then cooled well at 15° for some hours and filtered, the alcohol being evaporated and tested for artificial colouring matters (see Artificial Dyes in Vol. II). As a rule imitation wax and wax substitutes are coloured with the so-called Soudan dyes, which are turned pink with hydrochloric acid.

**Detection of Beeswax in Mixtures with other Substances**.—Beeswax is often contained in waxes of different kinds, such as paraffin

insect wax, which contains very little alcohol.

(a) BY MEANS OF THE ACETYL NUMBER. The substance and the unsaponifiable part extracted by the usual method by Leys' method (*see* 8) and its acetyl number determined (Methods, II). If this number is found to be zero, the presence of wax may be excluded; if, however, there is an acetyl number, the wax may be assumed and the amount may be calculated from the fact that the mean acetyl number of the higher wax is 122 and that the wax contains, on the average, about 10% alcohols.

(b) BY TRANSFORMATION OF THE MYRICYL ALCOHOL INTO MYRICYL ACID. 5 grams of unsaponifiable substance, extracted and dried, are intimately mixed with about 10 grams of lime and a little caustic soda, the mixture being placed in a flask and this plunged into a sand-bath and heated to 200–220°C. the temperature is measured with a thermometer immersed in the mixture and used at intervals as a stirrer. When cold, the substance is extracted with petroleum ether, the solvent evaporated and the residue weighed. If the weight is equal or nearly equal to that of the substance, the presence of wax is excluded, but if the petroleum ether extract is less in weight than the substance taken, wax may be present. In the latter case the difference between 5 grams (weight of substance) and the weight of the residue represents the myricyl alcohol contained in 5 grams of unsaponifiable matters. If, then, the percentage of unsaponifiable matter in the substance is known, the myricyl alcohol present in 100 parts of the substance itself and hence approximately the percentage of the wax present may be calculated, since 38 parts of myricyl alcohol correspond on the average with 100 parts of beeswax.

\* \* \*

The purity of a wax is judged first of all from the results of the various tests and the nature of the wax: if all or some of these characters lie outside the limits indicated in Table XLIX, the wax is not genuine.

A low specific gravity indicates the presence of solid paraffin, stearic acid or tallow, and a high one that of carnauba wax, Japan wax, etc.

The acid, saponification, ester, ratio, iodine and refractive index are also influenced more or less by the presence of various foreign matters, as is shown in the following table (page 439), where the mean values for ordinary virgin wax are compared with those of the substances commonly employed to adulterate it.

It should, however, be noted that mixtures may be prepared

	Gravity at 15° C.	Melting Point	Acid Number	Saponi- fication Number	Ester Number	Ratio Value	Iodine Number	Refracto- metric Degree at 40° C.
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>
ax . . .	0.964	63°	20	95	75	3.70	10	44
wax . . .	0.970	82°	0	63	63	63	—	46
ba wax . .	0.995	85°	4	79	75	18.75	10	66
wax . . .	0.990	53°	20	220	200	10	9	47
e. . . . .	—	below 55°	195	195	0	0	—	—
. . . . .	0.948	42°	4	195	191	48	40	47
colophony)	1.100	above 70°	180	190	10	0.06	115	—
paraffin . .	0.870	below 65°	0	0	0	0	0	22
e. . . . .	0.920	above 60°	0	0	0	0	0	40

## WOOL FAT

is obtained from wool by washing with soap or alkali carbonate or by extracting with a solvent (carbon disulphide or benzine). The crude fat is utilised especially for the preparation of lanoline and wool fat, from which wool fat oleine and stearine are prepared. Other products are dealt with in the next chapter (Industrial Products and the Treatment of Fatty Matters) ; here we shall deal only with crude purified wool fat and lanoline.

### A. Crude Wool Fat

It has a tallowy consistency, a yellow or brown colour, and a peculiar, rancid odour. It is slightly soluble in alcohol, and more so in ether, benzene, etc. ; it saponifies with difficulty. Its physical and chemical characters are given later in Table XLIX, dealing with animal fats.

It is dextro-rotatory ( $[\alpha]_D^{35} = \text{about } 6.9^\circ$  in chloroform solution), and its acid number may vary from about 10 to 50 (5-25% of free acids calculated as oleic acid) according to the method used in its extraction. On saponification it leaves little ash (1-5%).

It contains marked quantities of unsaponifiable substances (40-50%), consisting mainly of cholesterol and ischolesterol, and consequently gives a reaction of these higher alcohols with chloroform and sulphuric acid (General Methods, 19, 1, Higher Alcohols). It may also contain water and various foreign impurities in varying quantities.

Crude wool fat is readily identified by its external characters and by its saponification reaction. In analysing it, it is usually sufficient to determine the extent of saponification, and to test with possibly the



is carefully poured on to 5 c.c. of conc. sulphuric acid, at the zone of the two liquids there is produced a bright brownish-red color which reaches its maximal intensity after 24 hours.

The most important tests to be made on *lanoline*, especially for pharmaceutical purposes, are :

**1. Water and Ash.**—10 grams are heated at 100–110° weight, the residue being carefully incinerated and the ash weighed.

**2. Acidity.**—As in General Methods, 7.

According to the Official Italian Pharmacopœia, the test is made by dissolving 2 grams of the lanoline in 20 c.c. of petrol ether, adding 2 drops of phenolphthalein solution and then 0.5 c.c. of a 1% sodium hydroxide solution : the liquid should be coloured a pale pink.

**3. Other Tests.**—The lanoline is heated with aqueous ammonia solution to ascertain if ammonia is evolved. 10 grams of lanoline are heated on the water-bath with 50 grams of water : a clear oil layer should form at the surface of the water. If the lanoline is impure a brown, turbid and frothy mass is obtained.

\* \* \*

Pure anhydrous lanoline should contain only traces of moisture. It should emulsify with water should contain not more than 3% of the latter. It should have little ash (at most 0.5%), give no acid reaction with litmus paper, correspond with the Official Italian Pharmacopœia test for ammonia, and no ammonia when heated with soda solution.

## Spermaceti

This is the solid portion obtained by cooling and pressing the oil contained in the cephalic cavity of the sperm whale or cachalot (*macrocephalus*) and allied species.

Refined or pure spermaceti of commerce is in white, hard, brittle masses (thin sheets), slightly fatty to the touch and almost odorless. In the air it becomes yellowish and rancid.

It dissolves in boiling alcohol, from which it crystallises on cooling. It is soluble also in ether, chloroform, benzene and carbon disulphide. It dissolves very slightly in cold 98% alcohol and is insoluble in water or in water. Its physical and chemical characters are given in the following table.

Spermaceti consists mostly of *cetin* (the cetyl ester of palmitic acid), m.pt. 53.5°, and contains 50–52% of unsaponifiable substance.

**Detection of Adulterants.**—Additions of ceresine or stearic acid (stearine), tallow and beeswax are made, but only the extraneous substances easily destroy the characteristic crystalline appearance.

Nature of Wax.	Specific Gravity.	Point °C.	Point. °C.	Reaction Reading.	Number A	Reaction Number.	Number E	E. A
<b>ANIMAL WAXES</b>								
ary beeswax.	15	0.941-0.976 (0.964)	60.5-66.5 (63)	60-61	16.7-23.6 (20)	88-106 (95)	65.9-85.0 (75)	28-4.5 (3.7)
shed in the sun.	15	0.964-0.973 (0.966)	63-64	61-62	19-23 (20)	90-98 (95)	71-76 (75)	3.7
shed chemically.	100	0.818-0.827	63-64	61-62	16.8-24 21-22	93-108 81	71-84 59-60	3-4 3
acted (with solvents).	15	0.949-0.984	59-72	—	15-28	64-102	49-78	24-3.4
wax (Chedda wax), crude	15	0.966	60-69 (63-64)	—	5-13 (7-8)	75-145 (100)	70-124 (93)	7-18 (13)
ata, <i>A. florea</i> , <i>A. indica</i>	15	0.926-0.970 (0.970)	81-83	80-81	0	63-93 (63)	63-93 (63)	63
(Chinese wax)	100	0.810	39-42 36-42	—	10-50 0-1	77-146 98-127 (100)	—	—
ude	15	0.973	44-55	43-48	0-5	108-135	—	—
ified (Anhydrous lanoline)	100	0.901-0.902	—	—	—	117-150 (132)	—	—
oil.	15	0.940-0.960	—	—	—	121-136	—	—
oil (Arctic sperm oil).	15	0.808-0.842	—	—	—	—	—	—
oil ( <i>don rostratus</i> )	100	0.875-0.890	—	—	—	—	—	—
VEGETABLE WAXES	15	0.833	—	—	—	—	—	—
wax	100	0.876-0.905 0.827	67-92	64-75	10-21	47-65	34-53	—
ia <i>antisiphilitica</i> )	15	0.950-0.993	83-86 (85)	80	4-8 (4-5)	79-95 (79-80)	75-80 (75-76)	18-19
certifera L.)	100	0.990-1.000 (0.995)	—	—	—	—	—	—
from the fruit of <i>Myristica</i>	15	0.920	102-105	—	—	—	—	—
( <i>Ceronylon andicola</i> )	15	0.992-0.995	79-81	—	—	109	—	—
( <i>Musa spec.</i> )	15	0.905-0.970	80-82	—	2-3	—	—	—
x ( <i>Raphia Ruffia</i> )	15	0.950	60	—	—	—	—	—

1 The numbers in brackets indicate the more common limits and mean values.

Methods, 4, 7, 8 and 19). Addition of stearine or wax gives a white solid, while that of tallow or other fat increases the saponification number; paraffin or ceresine lowers the saponification number and increases the amount of unsaponifiable matter.

The two following tests are prescribed by the Official Italian Pharmacopœia :

1. SOLUBILITY IN BENZENE. 1 gram of the spermaceti is dissolved in 3 grams of benzene at a gentle heat : on cooling the liquid becomes clear.

2. TEST FOR STEARIC ACID. 1 gram is boiled with 10 c.c. of alcohol and 1 gram of dry sodium carbonate, and filtered. The filtrate when acidified with a dilute acid, should become barely opalescent, no precipitate indicating the presence of stearic acid.

\* \* \*

According to the Official Italian Pharmacopœia, pure spermaceti should have no odour of fish, should have a specific gravity 0.940–0.950, should melt at 50–54° or, if recrystallised from alcohol, at 54–55°; the acid reaction should not have an acid reaction; tests 1 and 2 should be performed.

## SPERMACETI OIL

This is the liquid part of the oil contained in the cephalopods, such as the cachalot and allied species.

The ordinary refined spermaceti oil of commerce is an almost colourless or pale yellow liquid, mobile and nearly odourless.

It is a liquid wax, consisting mostly of esters of one or more higher alcohols with fatty acids of the oleic acid series (fisetoleic acid). It contains 37–45% of higher alcohols (unsaponifiable substances) and 55–63% of fatty acids combined with these alcohols; it contains a small amount of free acids and it turns rancid with age. Its characters are shown in Table XLIX.

**Detection of Adulterations.**—Adulteration with mineral oils is common. These may be detected by determining the saponification and iodine numbers, and unsaponifiable substances. In mind the following :

1. MINERAL OILS. These lower the saponification number and increase the content in unsaponifiable substances. If the latter are dissolved in acetic anhydride and then cooled, the mineral oils separate completely from the liquid (*see* General Methods, 19).

2. FATTY OILS. These raise the specific gravity and the saponification number and diminish the proportion of unsaponifiable substances.

## CHAPTER X

### INDUSTRIAL PRODUCTS

#### FROM THE TREATMENT OF FATTY MATTERS

most important industrial products obtained from the treatment of fatty matters are : boiled linseed oil, oxidised oils, hardened or hydro-oils, Turkey-red oils, oleine, stearine, candles, soap and glycerine. The methods of analysis used for these materials are largely those employed with fatty substances, being based mainly on the determinations of various characters (specific gravity, melting point, acid number, saponification number, iodine number, etc.), for which the general methods of the preceding chapter are used. Any special tests necessary are described, and this section offers, in the following articles.

#### BOILED LINSEED OIL

Boiled linseed oil is fluid but more viscous than the crude oil, and is a less brownish-yellow or brown and of a peculiar odour ; there is no free fatty acid, and it is of a very thick, almost pasty form, which is brown with a greenish fluorescence and has a very marked odour.

In general, the boiled oil is distinguished from the ordinary or crude oil by the appearance, the smell, the high specific gravity (0.937-0.99), the absence of drying agents (these are sometimes absent, in which case the distinction is readily made by other characters) and especially by the fact that it dries.

Boiled linseed oil may be found mixed or adulterated with resin, resin oil, mineral oil, fish or blubber oil, or vegetable oil (colza, soja bean, etc.).

Analysis includes the following determinations and tests :

**Specific Gravity, Iodine Number, Saponification Number, Acid Number.**—By the general methods given in the preceding chapter.

Oil boiled with resinsates naturally contain small quantities of resin. The oil should be dried in a vacuum or by the use of a desiccant. Addition of resin should be assumed if the alcoholic extract is large in amount and the acid number of the oil is high (at least above 12; see later).

**5. Detection of Siccatives.**—This may be made on the oil or by dissolving the oil in ether and shaking with dilute nitric acid solution being tested by the ordinary methods for iron, manganese, calcium, zinc and cobalt.

**6. Drying Properties.**—A drop of the oil is spread on a glass plate ( $5 \times 10$  cm.) and left in the air, protected from dust, at  $15-20^{\circ}$ . From time to time the course of the drying is tested by touching the oily layer hard with the finger: drying is complete when the oil no longer adheres to the surface. The latter is then heated to  $100^{\circ}$  if cracking occurs.

Further, 25 parts of the oil are mixed intimately with 20 parts of white or minium, the paste thus obtained being spread on an iron plate and left to dry as before.

\* \* \*

Good boiled linseed oil should satisfy the following requirements:

That boiled at a moderate temperature should be only slightly yellow and should yield a perfectly white paste when mixed with pure white.

Its specific gravity should not be below 0.935 and as a rule is between 0.935 and 0.948, but oil heated at a very high temperature (and burned) may have a value as high as 0.99. The presence of adulterants (vegetable, animal, mineral) lowers the specific gravity.

The *iodine number* may vary from 150 to 172 in light boiled oil and fall to  $70^{\circ}$ , with those strongly boiled and dense.

The *saponification number* should lie between 190 and 195, but may be raised by colza oil and especially by mineral or resin oil.

The *acid number* should not exceed 12 (usually it stands between 8 and 10) and is raised by free resin.

It should not contain *foreign oils* or free *resin*.

The content of *unsaponifiable substances* should not exceed 2%.

The amount of *dryer* should be such that the oil does not lose more than 1% of ash.

In the *drying test*, pale oils should dry completely within 20 hours and dark ones within 12 hours. After being heated at  $100^{\circ}$ , the dry layer should not exhibit cracking and should become detached in scales when scraped with a knife. When mixed with zinc white or minium, it should dry completely within 24 hours.

are obtained by passing a current of air through a fatty oil at a temperature of about  $70-120^{\circ}$  until the oil becomes thick and viscous like pitch. Colza, cottonseed, maize, foot and fish oils are usually employed for this purpose.

In general, blown oils are dense, viscous, reddish-brown liquids with a pitchy odour (of boiled oil). In comparison with the corresponding original oils they have high specific gravities, refractivities and saponification numbers and low iodine numbers (see Table, p. 446). Further, they contain large quantities of hydroxy-acids, and it is characteristic of them that they furnish deep brown fatty acids (almost black with blown fish oils), which are partially soluble in ether.

The analysis of these products is concerned principally with the two following

**Origin of the Blown Oil.**—It is somewhat difficult to state the origin of the original oil from which a blown oil is prepared, since the specific reactions no longer hold. An approximate orientation may be obtained by means of the following criteria.

Fatty acids of oxidised *colza* oil are liquid and their lead salts are soluble in ether.

Fatty acids of oxidised *cottonseed* oil are solid and their lead salts are soluble in ether.

Fatty acids of oxidised *fish* oils are blackish and saponification of these oils yields a black, pitchy substance insoluble in potash, alcohol or ether and similar to the linnoxyn of linseed oil. This does not occur with vegetable or foot oils. Blown fish oils are the ones showing the greatest density accompanied by the highest iodine number.

Oxidised *foot* oils exhibit a specific gravity equal to that of oxidised vegetable oils but a less iodine number.

**Mixtures of Blown Oils with Mineral Oils.**—Mixtures of heavy mineral oil and oxidised oil (about 5-30%) form good lubricants for marine engines.

These products are recognisable by the smell and by the following test: 10 gms of the oil are saponified with 25 c.c. of alcoholic potash in the water-bath, heating for half an hour on the water-bath in a reflux apparatus with frequent shaking. Without evaporating the alcohol, the whole is transferred to a separating funnel, diluted with 150 c.c. of water, shaken and allowed to settle, and carefully and left to stand until sharp separation into two layers has taken place, the lower aqueous layer being then run off and the supernatant oil collected separately (with the help of a little ether), dried and

		Specific gravity at 15°.	Zeiss butyro- refracto- meter Number at 15°.	Saponifi- cation Number.	I N
Colza oil	{ ordinary .	0·912-0·917	68-69	176-181	9
	{ blown .	0·967-0·977	80	197-208	4
Cottonseed oil	{ ordinary .	0·922-0·925	68	191-198	10
	{ blown .	0·972-0·979	80-81	213-226	5
Ox-foot oil	{ ordinary .	0·921	62	194	
	{ blown .	0·972	73-74	241-242	
Fish oil	{ ordinary .	0·925	78	190-191	
	{ blown .	0·980-0·985	90-91	247-248	7

## HARDENED OR HYDROGENISED OILS

These are obtained by subjecting liquid fatty oils, either animal, to the action of hydrogen at a temperature of 130-150° in the presence of a catalytic substance, usually finely divided reduced nickel, platinum and various metallic oxides. The unsaturated ligands (oleic, linoleic, etc.) of the glycerides of the oils are transformed into stearic acid, so that the oils themselves become solid.

These products, marketed under the names of *Talgol*, *Canolol*, etc., are usually obtained by hydrogenising marine animal oils (e.g. whale oil), but they may also be prepared from vegetable oils (e.g. soja-bean, castor, etc.).

As a rule, hardened fats are solid and of the consistency of tallow. After very prolonged hydrogenation they acquire the hardness of tallow; they have persistent colours, odours and tastes which are very different from those of tallow but no longer recall the original oils. They usually melt at temperatures 2-3° below the points of fusion of the corresponding fatty acids but the strongly hydrogenised ones have still higher melting points. Fatty acids melt at temperatures 2-3° below the points of fusion of the corresponding neutral fats. Their acid number is small and their saponification number is normal (190-195), while the iodine number depends on the degree of hydrogenation and may fall to a few units.

Hydrogenised oils give the general colour reactions of tallow and are very similarly to the latter: thus, they give Hauchecorne's reaction and Bellier's reactions if they are derived from vegetable oils.

(mostly nickel) are found. analysis of these products includes :  
**Characters and Origin.**—Of the characters of hardened oils, those of importance, besides the objective ones, are the melting point, the melting point of the fatty acids (titer) and the acid, saponification and iodine numbers.  
To ascertain the origin of a hardened oil, the unsaponifiable substances must be extracted and identified (*see* Hog's Fat) : hardened animal oils contain cholesterol and the vegetable ones, phytosterol. The Fortelli and Jaffe reaction (*see* p. 430) indicates if a hardened oil is derived from a marine animal oil.

**Test for Traces of Catalyst (Nickel).**—This may be made on the whole product or, according to Fortini, in the following way : 5 to 10 grams of the fat are heated for half an hour on the water-bath with as much conc. hydrochloric acid, with frequent, vigorous shaking ; it is then filtered through a moist filter into a dish, evaporated to dryness and the residue moistened with a few drops of 1% alcoholic dimethylglyoxime solution : in presence of nickel a red coloration is obtained, this is rendered more evident when the solution is made slightly alkaline with a drop of dilute ammonia.

If the extract of the acid is highly coloured it is well to redissolve it in water and decolorise with animal charcoal.

## TURKEY-RED OIL

It is obtained by treating castor oil with sulphuric acid, eliminating the excess of acid by washing with water and sodium sulphate solution and neutralising more or less completely with ammonia or soda. It contains, therefore, essentially of *ammonium* or *sodium sulphuricinate*. It is a yellow liquid with the odour of castor oil. It dissolves in a small amount of water but further addition of water (10 vols. per 1 vol. of the oil) forms a perfect, white emulsion which persists for some hours and is neutral to litmus paper. Sulphuricicates neutralised with ammonia do not dissolve, however, in water in all proportions, but faint acidification of the emulsion with a few drops of acetic acid results in emulsification. If a large amount of acid or sodium chloride is added, either to the emulsion or to the solution of a sulphuricinate, an oily layer separates. Sulphuricicates are also completely dissolved by ammonia, the solution becoming rendered turbid by dilution with water. Alcohol, too, completely dissolves them.



chinate or sulphinate.

Analysis of Turkey-red oil comprises the following determinations, the second and fifth being of special importance for the quality of the product.

**1. Solubility and Emulsivity.**—2 or 3 c.c. of the oil with much water should give complete solution and addition of more water should then yield a persistent homogeneous emulsion. No acid reaction.

Dilute ammonia should also dissolve the oil completely and the solution should remain clear on dilution with a large quantity of water.

**2. Total Fat.**—10 grams of the oil are heated somewhat in a round-bottomed flask with 50 c.c. of water, 25 c.c. of dilute hydrochloric acid (1:1) is added and the liquid boiled for 3-5 minutes (until the fusible residue is clear), allowed to cool, transferred to a separating funnel, the flask is washed with a little water and with 200 c.c. of ether. The mixture is vigorously shaken and allowed to stand, the acid aqueous solution is removed and the ethereal solution washed with three successive portions of 15 c.c. of water, these wash waters being added to the aqueous solution and this kept for the determination of the sulphuric acid. The bulk of the ether is distilled from the ethereal solution in the flask and the residue transferred to a tared beaker; when the bulk of the ether has evaporated, the residual mass is dried for 1-2 hours over a naked flame (a medium flame being passed under the beaker when the fat ceases to froth) and then for half an hour in an oven at 105°C. The weight of fat thus found, multiplied by 10, gives the percentage of total fat in the oil.

The fat may then be used for investigating the nature of the oil (see below).

**3. Determination of the Sulphuric Acid.**—The sulphuric acid obtained as above is precipitated with barium chloride, the weight of the sulphate thus precipitated corresponding with the *total sulphuric acid* in the oil.

On the other hand the *sulphuric acid as ammonium or sodium sulphate* is determined by treating 10 grams of the oil with saturated sodium sulphate solution (quite free from sulphate), filtering through a moist filter, washing well with the saturated sodium chloride solution, diluting to 100 c.c. and precipitating the sulphate in it with barium chloride.

Subtraction of the percentage of  $\text{SO}_3$  as ammonium or sodium sulphate from the total percentage gives the *sulphuric acid (as  $\text{SO}_3$ )* as a percentage and this, multiplied by 4.725, gives the percentage of *sulphuric acid* in the oil.

number above 70 and an acetyl number below 140 show immediately that the oil has not been obtained from pure castor oil. The specific colour of the different oils (cottonseed, sesamé, etc.) may then be tried. It is also to be borne in mind that the emulsive oils prepared with olive, rapeseed, colza, sesamé and similar oils do not usually give clear solutions in alcohol, as does pure emulsive castor oil.

In detecting mineral or resin oils the saponification test is made.

**Ammonia or Soda.**—From 7 to 10 grams of the oil are dissolved in ether and the solution extracted four successive times with dilute sulphuric acid (1 part of conc. acid and 6 parts of water). The acid liquids are distilled with excess of caustic soda—when ammonium sulphoricinate is concerned—and the ammonia absorbed in standard acid; with sulphuric acid, the acid liquors are evaporated to dryness and the residue weighed as sulphate.

**Iron.**—The oil is shaken with dilute sulphuric acid and a few drops of potassium ferrocyanide solution, ether being then added and the liquid shaken and then left to stand. If iron is present, a more or less intense blue appears at the zone of contact of the two liquids.

\* \* \*

Turkey-red oils, prepared from castor oil, usually contain 45-60% of fatty substance (the rest being water), but there are more concentrated oils with 85-90% of fat (double oils). Those with about 45% of fat have a specific gravity 1.017-1.035 at 15°. The greater part of the fat consists of insoluble sulpho-acids and a small part of soluble sulpho-acids; neutral fat is present only in small proportion (1-2%). No iron should be present.

## OLEINE

### (Oleic Acid)

Oleine consists of the liquid fatty acids (mainly oleic acid)—more or less completely separated from the solid acids—yielded by animal tallow, bone tallow, vegetable tallow, palm oil and other fats. According to its method of preparation, it is distinguished as *oleine of saponification* and *distillation* (the latter, unlike the former, usually contains a large proportion of hydrocarbons resulting from the method of its preparation). In either case it is a brownish-yellow or brownish-red liquid, with a peculiar odour, soluble in 85% alcohol, acetic acid or petroleum ether.

The most important determination to be made in commercial oleines is the following:

**Acid, Saponification, Ester and Iodine Numbers.**—These are determined by the ordinary methods already described in the preceding

To separate and estimate the unsaponifiable substances, indicated on p. 388 are used.

To ascertain if the unsaponifiable matter is composed of carbons naturally occurring in distillation oleine or of added material, the rotatory power and the iodine number of the unsaponifiable matter are determined: in the former case the value of  $[\alpha]_D$  is from + 4 to + 10 and the iodine number 62-69, whereas mineral oils have no rotatory power or iodine number.

**3. Determination of the Solid Fatty Acids (Palmitic and Stearic).**—This may be effected by the methods indicated in the preceding chapter (p. 384) or by determining the *solidifying point of the oleine* (chapter, p. 418). From the point of solidification obtained, the percentage of stearine is deduced by means of de Schepper and Geitel's table, which has been prepared with the aid of mixtures of pure oleine with stearine of point 5.4° and stearine with solidifying point 48°:

TABLE L  
Content of Stearine in Oleine

Solidifying Point (° C.).	Percentage of Stearine (48°).	Solidifying Point (° C.).	Percentage of Stearine (48°).	Solidifying Point (° C.).
6	0.3	15	6.6	23
7	0.8	16	7.7	24
8	1.2	17	8.8	25
9	1.7	18	9.8	26
10	2.5	19	11.2	27
11	3.2	20	12.1	28
12	3.8	21	13.2	29
13	4.7	22	14.5	30
14	5.6			

\* \* \*

A good oleine should have an acid number about 179, corresponding to about 90% of free fatty acids, calculated as oleic acid. Oleines are usually found with 80-98% of free acids.

The content of neutral fat may vary from 0 to 20% (usually 10-15%).

The iodine number is usually 80-90. If it exceeds 90, the presence of linolenic and other less saturated acids derived from drying vegetable oils is indicated.

The unsaponifiable substances should not exceed 2% in saponifiable oils but may reach 10% in distillation oleine.

is the liquid part of distilled wool fat, consisting of free fatty acids (6), hydrocarbons and a little cholesterol and isocholesterol.

a more or less turbid liquid of a reddish-brown colour and more fluorescent and with a peculiar odour recalling that of wool fat. It is soluble in 95% alcohol, ether, benzene, etc.

On treatment with conc. sulphuric acid, its chloroform solution gives a red coloration and green fluorescence (cholesterol). It may be adulterated with mineral oils or resin.

Analysis includes the following:

### **Acid and Saponification Numbers and Unsaponifiable Matter.**

made of the methods described in the preceding chapter (General Methods, 7 and 19).

**Mineral and Resin Oils.**—From 50 grams or more of the oleine unsaponifiable substances are extracted by the ordinary methods, and the specific gravity, index of refraction, rotatory power (in about 3–4% solution and in a tube 10 cm. long at a temperature of 18–20°) and iodine number determined.

The presence of mineral oil may be presumed when these unsaponifiable substances have very low rotatory power and iodine number. The presence of resin may be recognised by the specific gravity being greater than that of the oil and the refractive index above 1.51.

**Resin.** The soap solution remaining after the separation of the unsaponifiable matter is decomposed with an acid and the fatty acids then separated by means of Morawski's reaction (*see* preceding chapter: General Methods, 20).

For the quantitative determination Twitchell's method (*ibid.*) is followed.

In applying Morawski's reaction, it is necessary thoroughly to separate the unsaponifiable matter in order to remove the cholesterol, which gives a reaction.

\*  
\* \*

Wool fat oleine should not contain more than 60% of unsaponifiable substances. These are liquid and have approximately the appearance of mineral oils. They should, however, have:  $D = 0.900-0.917$ ; refractive index (at 20°)  $n_D^{20} = 1.49-1.51$ ;  $[\alpha]_D^{20} = +15^\circ$  at least (in exceptional cases as low as  $+10^\circ$ ); iodine number  $= 50-80$ .

## STEARINE

(Stearic Acid)

to the feel and soluble in alcohol, especially in the hot.

Analysis of commercial stearines comprises principally the

**1. Solidifying Point (Titer).—**This is determined by Dali (see p. 418), the content of stearine being deduced by means of the corresponding table; when, however, fatty acids alone are concerned, the number given in the table is multiplied by  $\frac{100}{95}$  (see p. 419).

**2. Acid, Saponification and Iodine Numbers.—**By the methods given in the preceding chapter.

The iodine number depends on the quantity of oleic acid (or iso-oleic acid) in the stearine and this may be calculated from the iodine number by means of the formula

$$O = \frac{100}{90} \times I, \text{ or } O = 1.11 \times I,$$

where O = oleic acid sought, I = iodine number of the stearine, and 90 is the iodine number of pure oleic acid.

**3. Detection of Various Extraneous Substances.—**Commercial stearines sometimes contain solid paraffin or ceresine, wool fat or carnauba wax. The presence of such substances may be detected by the following rule when the acid number of the stearine is less than 195, which has been proved definitely as follows:

(a) A few grams of the stearine are digested in the hot with alcohol. If the substance does not dissolve completely, the liquid is allowed to settle and filtered and an examination made of the insoluble part. This part may contain solid paraffin or ceresine, beeswax or carnauba wax, the presence being indicated by the melting point, the acid and saponification numbers, etc. (see articles on Paraffin Wax, Ceresine and Beeswax).

(b) A quantity of the stearine is hydrolysed with alcoholic potash. The unsaponifiable substances extracted and examined by the method given on p. 388 *et seq.*; the presence of cholesterol will indicate the presence of wool fat stearine in the substance.

If then it is necessary to determine the various acids composing the stearine (stearic, palmitic, oleic) and to test for stearylactone, the methods given in the preceding chapter (see pp. 384 and 383) may be followed.

Finally, when the presence of lactones is excluded, that of ester may be deduced from the ester number and may be confirmed by saponification for glycerine (see p. 384).

\*  
\* \*

Commercial stearines usually solidify between 48 and 55° (the temperature for saponification stearine being somewhat higher than that for

## WOOL FAT STEARINE

is the solid part of distilled wool fat and consists of fatty acids and unsaponifiable substances (hydrocarbons, cholesterol).

According to the consistency, it is distinguished as *Soft stearine*, melting at  $55^{\circ}$ , and *Hard stearine* or *Wool fat wax*, melting above  $45^{\circ}$ .

In general, these products have a waxy appearance, a yellow or brownish color and a pronounced odour of wool fat, and they are soluble in hot alcohol and in ether, benzene or chloroform. When treated with concentrated acetic acid, the chloroform solution turns red and afterwards violet green fluorescence (cholesterol).

Analysis of wool fat stearine includes determinations of the melting point, acid number and content of unsaponifiable substances, as well as of the added hydrocarbons (vaseline, paraffin wax) or resin.

**Vaseline or Paraffin Wax.**—The unsaponifiable substances from the stearine are boiled for 2 hours in a reflux apparatus with an amount of their weight of acetic anhydride. The product is then washed repeatedly with boiling water until the reaction is neutral and in one part the acetyl number is determined (see p. 378). Another part (about 5 g.) is boiled with 50 c.c. of 90% alcohol, the liquid being filtered off and the residue boiled with 40 c.c. and then with 30 c.c. of 90% alcohol. The part insoluble in alcohol, which consists of hydrocarbons alone, the specific gravity, rotatory power (in benzene solution at about  $20^{\circ}$ ) and acid number are determined.

**Resin.**—This is tested for as in wool fat oleine (see p. 451).

\*  
\* \* \*

According to Marcusson and Skopnik<sup>1</sup> and to Coen,<sup>2</sup> wool fat stearines melt between  $40^{\circ}$  and  $65^{\circ}$ ; they contain 56–90% of free acids (calculated as stearic acid) and 9–42% of unsaponifiable substances, which are brown, fluorescent or semi-liquid masses with a faint aromatic odour and have the acid number about 25–37, the  $[\alpha]_D^{20}$  +  $12^{\circ}$  to +  $30^{\circ}$  and the iodine number

the portion of the unsaponifiable matter which does not combine with acetic anhydride (hydrocarbons free from higher alcohols) has  $D = 0.907$ – $0.910$ ,  $[\alpha]_D^{20} = +12^{\circ}$  to +  $21^{\circ}$ , and iodine number = 26–54.

The presence of extraneous hydrocarbons may be suspected when the acetyl number of the unsaponifiable substances is less than 25 and the portion of them which is combinable with acetic anhydride has a specific gravity less than 0.9,  $[\alpha]_D^{20}$  less than +  $12^{\circ}$  and an iodine number less than 26.

portions of mineral substances (soda, lime, sulphates), residues (hide, membranous fragments) resulting from the preparation.

This product forms a fairly dense, almost pasty, yellow or orange mass which has a special odour recalling that of fish oil and remains homogeneous even on long standing.

*Artificial dégras* is obtained by mixing natural dégras with fish or resin oil, vaseline, wool fat, tallow, etc., or by artificial oxidation of oils, followed by emulsification with water and sometimes by the addition of the other extraneous substances mentioned above.

Artificial dégras is also a yellow or orange dense liquid, which is more liquid than the natural product and has a peculiar fishy odour; on long standing, it tends to divide into two layers, the water being at the bottom.

Analysis of dégras includes various determinations and tests which serve as a guide in ascertaining if it is a natural or artificial product, and, that is, based solely on fish oils, or if it is mixed with tallow, wool fat, oils, vaseline or resin oils, these being the most frequent adulterations of dégras.

The principal determinations are as follows :

**1. Water.**—10 grams of the dégras are placed in a porcelain dish previously heated to redness with about 10 grams of coarse sand and tared ; the fat is mixed well with the sand and the dish allowed to cool and dried at 120° until of constant weight (4-5 hours). The loss on drying gives the water.

**2. Non-fatty Substances (Organic Residues).**—20 grams of dégras are dried in an oven at 120° or even over a direct flame, the liquid being stirred with a thermometer and care taken that its temperature does not exceed 105° ; the dried product is dissolved in petroleum ether and the solution filtered through a tared filter, the insoluble matter washed with petroleum ether and then with a little ether or benzene, dried at 100° and weighed.

This insoluble matter consists principally of epidermis and hair, which is readily recognisable with a lens or microscope, together with a few impurities.

On the other hand, evaporation of the petroleum solution and drying of the residue dried at 105° gives the total fat ; the latter is used for the determinations indicated under 4 (below).

**3. Ash.**—10 grams of the dégras are carefully heated in a porcelain dish over a naked flame until copious fumes are emitted, the residue is then heated more strongly on a sand-bath and finally in a muffle

2). From the acid number the percentage of free acids expressed as acid (see p. 374) is calculated.

**déragène.**—This is the special resinous substance formed by the saponification of the fish or blubber oils<sup>1</sup> and is what gives *body* to the dégras, its power of emulsivity with water and renders it specially adapted for the treatment of skins. It is determined as follows<sup>2</sup>:

10 grams of the dégras, either as it stands or after drying at 100° as described under 2 (above), are dissolved together with 7 grams of caustic soda in 10 c.c. of water and 50 c.c. of alcohol, the solution being heated on a water-bath in a reflux apparatus until saponification is complete (about 1 hour).

The alcohol is then expelled, the soap dissolved in water and separated by the addition of hydrochloric acid, and the whole boiled until the mixture of oil and déragène becomes quite fluid. When cool, the mass is poured into a separating funnel and the flask rinsed out with about 150 c.c. of petroleum ether boiling below 75°; the whole is well shaken and allowed to stand until the aqueous acid liquid separates sharply from the oil solution, the former being then run off. The funnel then contains a petroleum ether solution of the fatty acids and of the unsaponifiable matter of the dégras, together with an insoluble, blackish, resinous substance constituting the déragène, which adheres well to the walls of the funnel. The petroleum solution may be poured from the top of the funnel without any of the déragène being lost. The déragène is then washed with a little petroleum ether and dissolved in hot alcohol, the solution being filtered if necessary, the alcohol evaporated and the residue dried at 100–105° and weighed.

**saponifiable Substances.**—According to Baldracco,<sup>3</sup> these are determined exactly as follows: 15–20 grams of the dégras are dissolved by boiling with 5 grams of caustic potash dissolved in 10 c.c. of water and 50 c.c. of alcohol for 2–2½ hours in a reflux apparatus, the solution is then transferred to a dish and the alcohol completely expelled by evaporation on a water-bath. The residue is well mixed with 8 grams of sodium bicarbonate and 50–60 grams of coarse quartz sand previously washed and calcined, and completely dried in an oven at 110°. The mass is broken into small pieces, placed in an extraction thimble and extracted with petroleum ether boiling below 75°.

The petroleum solution is washed several times with water in a separating funnel, the water then evaporated, the residue, when dried at 110° and weighed, represents the unsaponifiable matter contained in the dégras.

The best proportions of déragène are furnished by whale oil and cod-liver oil, and therefore, the best dégras.



contains wool fat, mineral oils and other unsaponifiable matter.

\* \* \*

Good *dégras* is golden-yellow or orange and homogeneous and translucent. Natural *dégras* usually contains 15–25% of *water*, while the artificial products contain 10–25%.

The other components may vary within the following limits, *referred to the dry dégras* (free from water):

The *non-fats* (various organic residues) may reach 8% in natural *dégras* (ordinarily 2–5%), but are less than 1% in artificial *dégras*.

The *ash* may amount to 5% with natural *dégras*, but is less than 1% in the artificial product; it should contain only traces of iron (not more than 0.05% of the original *dégras*).

The *free fatty acids*, calculated as oleic acid, may vary from 2% in natural *dégras*, but are usually less than 20% in the artificial product.

The *saponification number* is above 200 (220–240) in natural *dégras*, but not less than 190 in artificial *dégras*. A value less than 190 (referred to the dry substance) denotes the presence of extraneous matter, such as resin oils, vaseline or wool fat.

The proportion of *dégragène* is somewhat variable, since it depends on the mode of preparation of the *dégras*. Usually natural *dégras* contain not more than 10% of *dégragène*, and the artificial product not more than 10% of *dégragène*.

The *unsaponifiable matter* does not exceed 3% in pure *dégras*, whether natural or artificial, but is considerably higher in products adulterated with resin oils, vaseline or wool fat.

## CANDLES

Three types of candles are usually sold: stearine, paraffin and beeswax.

*Stearine candles*, which are opaque and white, should be made from pure stearine (mixture of stearic and palmitic acids, etc.; see Stearine). Very often they contain a certain quantity of paraffin wax, and sometimes ceresine or a small quantity of carnauba wax (high melting point).

*Paraffin candles*, which are translucent and white, are made from paraffin wax with a high melting point (about 50°), usually with the addition of 3–15% or even more (up to about 33%) of stearine, such being called *composite candles*.

*Wax candles*, which are yellowish and opaque and possess the characteristic odour of wax, should be made from pure beeswax, but nowadays usually made from mixtures of wax, paraffin wax, and stearine, the wax being present often in small amount.

Analysis of candles is usually made with the object of determining their composition, but includes also tests of the illuminating power.

the quantitative determinations it is well to melt a whole candle and take various pieces taken from several candles at different points in order to obtain a homogeneous and representative sample.

It is further necessary to determine the weight of the *wick*, several pieces being broken from one or more candles and weighed and the wick carefully separated and weighed: the weight of the wick is referred to 100 parts of candle.

The commonest cases of analysis of candles are the following:

**MIXED STEARINE AND PARAFFIN (OR CERESINE) CANDLES.** About 5 gms. of the sample are heated and shaken with 50 c.c. of 90% alcohol in a water-bath, the liquid being subsequently titrated with decinormal potassium hydroxide in presence of phenolphthalein: 1 c.c. N/10-KOH = 0.1125 gm. of stearine (mean molecular weight of ordinary stearine = 270). The liquid is then again heated on the water-bath for about an hour, with frequent shaking, with 4-5 c.c. of concentrated potassium hydroxide in order to saponify the small quantity of neutral fat or any lactones present in the stearine (for greater precision the saponification number also may be determined). The solution is then diluted with water and allowed to stand until the paraffin is thoroughly solidified to a *solid disc*, the aqueous solution being then decanted off and the paraffin washed several times with water, being heated and cooled each time. The washed paraffin is finally dried in a dish, dried in an oven at 105° and weighed.

The paraffin thus separated is then tested for ceresine by the methods given on p. 364.

The stearic acid (stearine) calculated from the acid number and the weight weighed directly are then referred to 100 parts of candle, allowance being made for the weight of the wick (*see* example given below for case *b*). For rapid, approximate determinations it is sufficient to calculate the weight of the acid from the acid number and the paraffin by difference.

**MIXED WAX, STEARINE AND PARAFFIN CANDLES.** In these candles it may be necessary to calculate either all three of the components or only the paraffin (or ceresine).

**Determination of all of the components.** The acid and saponification numbers are determined in the usual way, the various components being calculated as in the following example.

**EXAMPLE:** The wick of a candle is found to represent 0.4% of the weight of the candle, while the wick-free mass has:

Acid number = 77.0  
Saponification     „     = 84.7,

Ester number = 77.

Weight of wax to be 55, the mean saponification

so that

$$y = 9.75.$$

This number  $y$  is deducted from the saponification number found in substance,

$$84.7 - 9.75 = 74.95,$$

and from this the stearic acid ( $z$ ) is deduced from the proportion

$$207 : 100 = 74.95 : z,$$

so that,

$$z = 36.11\% \text{ of stearic acid.}$$

(c) The solid paraffin is then given by difference,

$$100 - (10.26 + 36.11) = 53.63\% \text{ of paraffin.}$$

(d) The composition of the entire candle (with the wick) is then

Wick.	.	.	.	.	.	.	.	0.40
Wax .	.	.	.	.	.	.	.	10.22
Stearic acid	.	.	.	.	.	.	.	35.96
Paraffin	.	.	.	.	.	.	.	53.42

2. *Determination of the paraffin (or ceresine) alone.* In this case the candle is cut into small pieces and the pieces are boiled for 3-4 hours with alcoholic potash in a flask with a long tube to act as reflux condenser and then left to cool. When the paraffin has set well at the surface of the liquid. The latter is then poured off together with all the unsaponifiable matters of the wax which are suspended in a flocculent form, care being taken that the whole of the paraffin remains in the flask. The paraffin is then again boiled for 3-4 hours with alcoholic potash, the whole being afterwards transferred to a separating funnel, hot to a separating funnel, the flask being rinsed out with boiling water so as to obtain all the paraffin in the funnel. The aqueous alcohol is run away and the paraffin remaining in the funnel washed several times with hot water and subsequently rinsed out into a small beaker with the help of very hot water. After cooling, the solid paraffin disc is weighed, 100-105° in a tared dish and weighed.

This paraffin is then tested for ceresine by the methods given for Paraffin wax and Ceresine.

2. **Illuminating Power.**—This is measured as with petroleum oil (see Chapter VIII, Lighting Oil, 7).

3. **Bending Test.**—This test, made especially with paraffin candles, consists in introducing the base of the candle into a suitable support so that the candle is horizontal and leaving it in a room at a constant temperature of 22-25° for some hours to ascertain if it becomes curved and to what extent. A standard candle is used for purposes of comparison.

neutral or only slightly alkaline, and this group includes, for toilet soaps in general, so-called Marseilles white soap and certain soaps.

Called "cold" soaps, obtained by saponifying fats with an alkaline without adding common salt, are usually very alkaline; they contain glycerine and all the impurities of the fats and alkali used. Potash soaps belong to this class.

Soaps are analysed to ascertain their composition and to see if they are adapted to definite uses. Analysis includes mainly determinations of water, total fat, alkali, resin, glycerine, etc.

**Sampling.**—The various determinations require at least 100 grams of soap which is stored in a well-dried and closed glass jar.

For analysis of soap in small pieces or cakes, these are cut into at least four parts (longitudinally and crosswise), from which thin shavings are taken and cut up, the whole being thoroughly mixed and a portion taken for analysis. For analysis of soap in blocks or large rectangular pieces, two triangular prisms with bases on two opposite sides are taken so as to represent proportionally the dried outer part and the more hydrated inner part; these are rapidly cut up, well mixed and the sample to be analysed then

For powdered soaps are well mixed with a spatula or in a mortar and a sample then taken.

**Water.**—In a platinum dish, tared with a glass rod, 5–8 grams of soap are weighed, the dish being then heated in an oven first at 60–70° and then at 100–105° until of constant weight, the mass being stirred from time to time with the rod. Loss of weight represents water.

For soft soaps or others containing a large proportion of water, a certain amount of siliceous sand or ground pumice, previously ignited, is tared with the soap with the glass rod.<sup>1</sup>

**Total Fat.**—20 grams of the soap, dissolved in water, are treated by excess of dilute sulphuric acid (1 : 3) or of normal sulphuric acid (also 4), the solution shaken with 100 c.c. of petroleum ether, b.p. 65°, and the acid liquid separated and again shaken with 100 c.c. of petroleum ether. The two petroleum extracts are united, washed with water, filtered (if necessary) into a tared dish and evaporated at a low temperature, the residue being dried in an oven at about 110° to constant weight.

This gives the total fat, which, besides the fatty acids and resin acids, may contain also neutral fat and unsaponifiable matter; it is therefore examined further (see below: 5, 8 and 11).

utilised for the determination of the alkalies (see 4).

**4. Total Alkalies.**—This determination may be combined with the preceding one of the total fat. For this purpose it is sufficient to add the aqueous solution of 20 grams of the soap with 100 c.c. of normal acid and then to proceed as in 3, care being taken to lose no trace of the aqueous acid liquid separated from the petroleum ether solution.

This liquid, collected quantitatively in a conical flask, is titrated with normal potassium hydroxide solution in presence of methyl orange.

The difference between the volume of normal acid added to the soap solution and the volume of normal alkali necessary to neutralise the soap solution, represents the total alkali—existing as hydroxides, silicates, borates and soaps—in the soap. This is expressed as potassium oxide for hard or powdered soap, and as potassium oxide for soft soap. 1 c.c. normal  $\text{H}_2\text{SO}_4 = 0.031$  gram of  $\text{Na}_2\text{O} = 0.047$  gram of  $\text{K}_2\text{O}$ .

**5. Alkalies combined with Fatty Acids.**—The alkalies combined with fatty (or resin) acids, that is, as soaps, are deduced from the difference between the number of the total fat obtained as in 3.

The acid number is determined as on p. 374, and the results are expressed as  $\text{Na}_2\text{O}$  for hard or powdered soap and as  $\text{K}_2\text{O}$  for soft soap.

**6. Free Alkalies.**—The presence of excess of alkali in a soap is determined (1) by dissolving 1 part of the soap in 50 parts of 95% alcohol and adding a few drops of phenolphthalein solution (red coloration), or (2) by adding a few drops of a solution of mercuric chloride to a section of the soap, recently cut, a drop of mercuric chloride solution (yellow coloration) or mercurous nitrate solution (black coloration).

Quantitatively free alkalies as hydroxide and as carbonate are determined as follows:

(a) ALKALIES AS HYDROXIDE. A solution of 10–15 grams of soap dissolved in 100 c.c. of absolute alcohol is neutralised, if necessary, with a few drops of alcoholic potash (phenolphthalein as indicator). The solution of the soap are then dissolved in it and 2–5 c.c. of cold, saturated strontium chloride solution added to precipitate the alkali carbonate. The free alkalinity being then titrated with standard alcoholic stearic acid solution in presence of phenolphthalein.<sup>1</sup>

(b) ALKALIES AS CARBONATE. If the soap does not contain silicates, borates or other alkaline salts, the alkalies as carbonate may be determined *indirectly* or *by difference*, by subtracting from the total alkali the sum of the alkali as hydroxides and that combined with the fatty acids (see 5 and 6a), all expressed as  $\text{Na}_2\text{O}$  or  $\text{K}_2\text{O}$ : this difference, expressed into  $\text{Na}_2\text{CO}_3$  or  $\text{K}_2\text{CO}_3$ , represents alkalies as carbonates.

When silicates, borates or other alkaline salts are present, the alkalies as carbonate are determined by difference, by subtracting from the total alkali the sum of the alkali as hydroxides and that combined with the fatty acids (see 5 and 6a), all expressed as  $\text{Na}_2\text{O}$  or  $\text{K}_2\text{O}$ : this difference, expressed into  $\text{Na}_2\text{CO}_3$  or  $\text{K}_2\text{CO}_3$ , represents alkalies as carbonates.

**Free Fatty Acids.**—These are determined only when the soap does not give an alkaline reaction.

5 grams of the soap are dissolved in neutral 60% alcohol and the solution is titrated with alcoholic decinormal caustic potash in presence of phenolphthalein. The acidity is expressed as oleic acid : 1 c.c. N/10-KOH requires 1.83 gram of oleic acid.

**Neutral Fat and Unsaponifiable Substances.**—From 6 to 8 grams of the total fat, extracted as in 3, are dissolved in about 50 c.c. of 95% alcohol and the liquid neutralised with seminormal alcoholic caustic potash in presence of phenolphthalein (to a faint pink coloration); it is then diluted with about 50 c.c. of water and extracted successively with 20 c.c., and 50 c.c. of petroleum ether (b.pt. not above 65°). The petroleum ether solutions are washed three times with three quantities of 20 c.c. of 58% alcohol and then evaporated, the residue being dried at 105° and weighed.

This gives the neutral fat plus any unsaponifiable substances contained in the soap.

In the absence of the latter (which may be detected by a separate test), the weighed residue must be saponified with alcoholic potash, the solution being diluted with petroleum ether in the manner described above, and the unsaponifiable matter extracted, representing the unsaponifiable substances, weighed. The amount of neutral fat is then given by difference.

**Resin.**—The presence of resin (colophony) in a soap is readily detected by the application of Morawski's reaction (*see* p. 390) to the fatty acids obtained from the soap itself, provided the latter does not contain water, in which case the test is made on the fatty acids after elimination of the unsaponifiable matter.

Quantitative determination of the resin is effected by Twitchell's method (*see* p. 390).

**Glycerine.**—This occurs in "cold" soaps and in soft or potash soaps (containing 5%), in which its presence is due to the method of preparation, and in transparent or glycerine soaps, to which it is purposely added. For its determination, 20–25 grams of the soap are dissolved in hot water, decomposed by means of dilute sulphuric acid and filtered to remove insoluble matters. The filtrate is neutralised, defecated with lead acetate, diluted to a definite volume and filtered, the glycerine being estimated in the filtrate by the dichromate method (*see* Glycerine).

If the soap contains ethereal oils, sugar, dextrin or other substance which is not removed by dichromate, this method is inapplicable. In such cases the aqueous liquid is evaporated with addition of lime and the glycerine

may contain resin and palm oil, and green or brown ones, s oil and resin. Further, the solidifying point, acid and iod and certain colour reactions and other investigations of the obtained from a soap give information, up to a certain point, acter of the fats used.

For example : Soaps prepared from oleine give fatty acids w at a low temperature and contain only small quantities of sol examination of these, *see* p. 384).

Soaps from coco-nut oil give fatty acids with an acid numbe and a low iodine number.

Those from linseed and other drying oils contain hydroxy-ac in the cold in petroleum ether and yield fatty acids with a number.

Soaps from cottonseed, sesamé and arachis oils give fatty show Milliau's and Villavecchia and Fabris' reactions and conta acid (*see* Cottonseed, Sesamé and Arachis Oils, preceding cha

Resin soaps give the reaction for resin with acetic anhydr phuric acid (*see* 9).

Tests for cholesterol and phytosterol (*see* Hog's Fat) show soap contains animal or vegetable fats.

**12. Extraneous Substances.**—These may be of varie and principally as follows :

(a) MINERAL SUBSTANCES. Alkaline chlorides, sulphates, and phosphates, water glase, borax, heavy spar, kaolin, talc, si pumice, tiipoli, etc. Some soaps (especially powdered) contain a agents, such as sodium peroxide, perborates, percarbonates and p

All these substances may be recognised and determined the soap with absolute alcohol and examining the insoluble re ordinary analytical methods, both qualitative and quantitativ

(b) VARIOUS ORGANIC SUBSTANCES. These may consist of : dextrin, sugars (saccharose, glucose, molasses), vegetable gu and casein. Such substances also remain undissolved when treated with absolute alcohol and may be detected in the resid of the microscope, by treating with iodine (starch, dextrin), by and reducing powers (sugars), by the way in which they bu etc.).

(c) ALCOHOL. About 50 grams of the soap are dissolved i tepid water and decomposed with a slight excess of dilute su and filtered. The filtrate (which should not be much more tha neutralised with potash and distilled, 100 c.c. of distillate bei From the density of this the alcohol is calculated as follows :

Identify nitrobenzene, the ethereal extract obtained in the above is dissolved in a little alcohol and a scrap of zinc and 2-3 c.c. of sulphuric acid added to the solution. After 2-3 hours the liquid is poured into a dish and the filtrate exposed for an instant to chlorine issuing from a test-tube containing a little potassium chlorate and conc. hydrochloric acid : a persistent violet coloration is produced (*Armani and Barboni*).

Soaps based on coco-nut or palm oil give, with steam, a small quantity of the acids of peculiar odour, which must not be confused with that of soap containing added perfume.

**MEDICINAL SUBSTANCES.** Medicinal soaps are made with the most valuable substances, mostly antiseptics, among which are formalin, phenol, eucalyptol, malene, tar, ichthyol, camphor, sulphur, salicylic and boric acids, mercuric salts, arsenical compounds, juices of medicinal herbs, etc.

These may be tested for by shaking the soap with ether, evaporating the etheral solution and examining the residue by suitable methods, or dissolving the soap in water, precipitating with barium chloride and filtering the barium soap thus formed with alcohol or ether.

Mercury and arsenic compounds, boric acid and the like may be detected by dissolving the soap with hydrochloric or nitric acid and then testing the acid aqueous liquid.

One of the commonest medicinal soaps contains carbolic acid. To determine the proportion of the phenol, 5-10 grams of the soap are dissolved in water with addition of caustic soda, the solution shaken with ether and the aqueous liquid treated with excess of sodium chloride to precipitate the insoluble mole of the soap. The liquid is then filtered and the insoluble residue dissolved with saturated sodium chloride solution, the liquid being then filtered and treated with dilute sulphuric acid and the phenol estimated by means of the ferric chloride test (*see Carbolic Acid*, p. 330).

**MINERAL AND RESIN OILS, PARAFFIN WAX, TURPENTINE, ETC.** These may be detected by extraction of the soap with ether. In most cases, mixtures of soap with mineral or resin oils, vaseline and the like, may be detected by the usual tests for lubricants or cart-grease, analysis of which is dealt with in the chapter on Lubricants (*see* p. 365).

## GLYCERINE

*Crude glycerine* (*saponification, soap-lye or distillation glycerine*) forms a yellowish or brown liquid with a repellent odour and an acrid taste, while *refined glycerine* (*refined, distilled or double distilled, for dynamite*) consists of a colourless or almost colourless, odourless, syrupy liquid with a sweet



salts (chlorides, sulphates, sulphides, thiosulphates, lithium and organic substances (soaps, tarry substances, proteins, etc.) analysis is usually restricted to determinations of the alkali (free or combined), free acid, residue on evaporation, water and glycerine.

**Sampling.**—The sample should contain portions from every part forming the parcel and should be taken, if possible, as soon as the material is filled, since crude glycerine often contains suspended matters which are gradually deposited.

If such deposition has already occurred, a good average sample may be obtained with the help of a special sampler.<sup>2</sup>

Note is made of any suspended matter observed while the sample is being taken, and also of the temperature and of the form and condition of the vessels when these are not similar.

**1. Ash and Total Alkali.**—From 2 to 5 grams of the glycerine are weighed in a platinum dish and evaporated carefully over a flame until the residue charred at the lowest possible temperature.

The carbonaceous mass is then extracted with boiling water, filtered and washed. The filter and the contained charred mass are ignited in the same dish, the aqueous extract and wash-waters being evaporated. The whole evaporated to dryness on a water-bath and again ignited so that the ash does not fuse.

The ash thus obtained is weighed and then dissolved in water and titrated with normal acid (indicator: methyl orange), the alkalinity being expressed as percentage of  $\text{Na}_2\text{O}$  in the glycerine.

**2. Free Caustic Alkali.**—20 grams of the glycerine are weighed in a 100 c.c. flask, dissolved in 50 c.c. of recently boiled water, treated with excess of barium chloride solution and 1 c.c. of alcoholic phenolphthalein solution, made up to volume with boiled water, shaken vigorously and allowed to stand at rest. Subsequently 50 c.c. of the clear liquid are pipetted off and titrated with normal acid. The free alkali is calculated as  $\text{Na}_2\text{O}$  per 100 grams of glycerine.

**3. Alkali as Carbonate.**—10 grams of the sample are dissolved in 50 c.c. of distilled water, treated with sufficient normal acid to convert the total alkali (*see* 1) and boiled in a reflux apparatus for 15–20 minutes. The condenser is washed down with recently boiled distilled water. The free acid titrated with normal soda in presence of phenolphthalein.

The result is calculated as percentage of  $\text{Na}_2\text{O}$  and from this the percentage of alkali is calculated.

<sup>2</sup> The methods were fixed in 1911 by an International Commission of Glycerine Analysts, consisting of English, German and French analysts, as a result of the Congress of Glycerine Manufacturers held in London in 1909.

ly.—Ten grams of the sample, dissolved in 50 c.c. of recently distilled water, are titrated with normal caustic soda in presence of phenolphthalein. The result is expressed as  $\text{Na}_2\text{O}$  necessary to neutralise the acidity of the glycerine.

**Residue at  $160^\circ$ .**—In a 100 c.c. measuring flask, 10 grams of the sample are weighed, diluted with a little water and treated with normal alkali (according as the sample is alkaline or acid) in such amount that the glycerine assumes an alkalinity corresponding with 0.2% of  $\text{Na}_2\text{O}$ . The solution is then made up to volume and shaken, 10 c.c. (or, if the sample is acid, a lesser quantity sufficient to give a residue not exceeding 0.2 grams) being transferred to a tared porcelain dish 12 mm. deep and 6 cm. in diameter. The bulk of the water is evaporated on a water-bath and the dish then placed in an air-oven ( $30 \times 30 \times 30$  cm.) furnished with a thermometer, rests on an iron plate 20 mm. thick, as half-way up a shelf covered with asbestos board on which the residue containing the glycerine rests. The latter is heated at  $160^\circ$  until thin vapour is emitted, then removed from the oven, cooled, 0.5–1 c.c. of water added and the contents gently mixed. The water is again evaporated on the water-bath and subsequently on the air-oven until the residue, placed within the oven, no longer froths. The process usually requires 2–3 hours.

At the end of the point the dish is kept in the oven at  $160^\circ$  for exactly one hour, then removed, allowed to cool in a desiccator over sulphuric acid.

The residue is next treated with water, re-evaporated, dried, and weighed for an hour as before, this procedure being repeated until the weight does not exceed 1–1.5 mgrms. per hour.

The weight of the residue at  $160^\circ$  is *corrected* for the acid or alkali added to give the alkalinity to the desired point. With acid glycerine, 0.022 is subtracted for each c.c. of normal alkali added. With alkaline glycerine the correction applied is that resulting from the transformation of  $\text{Na}_2\text{CO}_3$  into  $\text{NaCl}$ . The corrected weight gives the residue which is calculated for 100 grams of the glycerine.

The residue is kept for the determination of any impurities capable of

**Organic Residue.**—The organic residue represents the difference between the residue at  $160^\circ$  and the ash.

It should, however, be noted that the  $\text{CO}_2$  formed for the transformation of organic acids during the incineration is not contained in the organic

**Preparation.**—On a clock-glass of about 15 c.c. capacity are placed 2–3 grams of the sample, which is then washed with acid and

again, the glass is left in the desiccator at the above pressure weight is constant (usually about 48 hours at 15° are required). of weight represents water.

**9. Glycerine.**—Either of two methods may be used <sup>1</sup>:

A. ACETYLATION METHOD, applicable to crude glycerine, provided it contains not more than 50% of water.

*Reagents required:*

(a) *Acetic anhydride* (puriss.), which should be carefully examined to purity and which in a blank esterification experiment should not require more than 0.1–0.2 c.c. of normal soda, and which should turn only slightly brown when boiled for an hour with sodium acetate.

(b) *Pure dry sodium acetate*, obtained by fusing the salt in a dish, powdering it rapidly and storing in a closed vessel in a desiccator. It should be absolutely free from moisture.

(c) *Normal caustic soda solution*, which should be very carefully prepared with well-boiled water and should be quite free from carbon dioxide.

(d) *Normal sulphuric acid*.

(e) *Phenolphthalein solution*, containing 0.5 part in 100 parts of alcohol and neutralised.

*Procedure.* In a round-bottomed flask of about 120 c.c. capacity, washed and dried, 1.25–1.50 gram of the glycerine is rapidly weighed, 10 grams of the sodium acetate and 7.5 c.c. of acetic anhydride being added. The flask is then connected with a small reflux condenser by means of a ground joint or a rubber stopper (the latter should be first put in after exposure to the vapour of boiling acetic anhydride) and the liquid is gently shaken for about an hour. It is then cooled somewhat and 50 c.c. of boiled hot water (at about 80°) added by way of the condenser. The liquid being shaken and heated, if necessary—but not above 80°—the solution is complete (excepting for a few black flocks due to impurities). The condenser tube is washed down with a little boiled water, detached and the stopper or ground joint also washed down. The liquid is filtered into a flask holding about a litre, the original flask and filter being thoroughly washed with boiled, cold water. 2 c.c. of phenolphthalein solution are next added and the liquid neutralised with the normal caustic soda solution (to a faint yellowish-red coloration), care being taken to shake the flask continually while the alkaline solution is run in from the burette.

After the neutral point is reached, a further quantity of 50 c.c. of normal caustic soda is added, the flask being then closed with a stopper and connected by a long glass tube to act as reflux condenser, and the liquid boiled

with crude soap-lye glycerine, when this contains more than 2.5% of free residue at 160° (see 7), the residue at 160° obtained as in 6 (above), is also be acetylated in the manner just described; if the result thus obtained corresponds with more than 0.5% of glycerine (on the residue), the excess over 0.5% is deducted from the percentage of glycerine in the sample itself.

For distilled saponification glycerine and the like, acetylation of the free residue is carried out when this exceeds 1%, the procedure being the same and account being taken only of the excess of glycerine over 0.5%.

**DICHROMATE METHOD.** *Reagents required:*

(a) *Potassium dichromate* (puriss.), powdered, dried at 110-120° and kept in a well-closed vessel.

(b) *Standard dichromate solution:* 7.4564 grams of dichromate (a) are dissolved in water to 1 litre.

(c) *Ferrous ammonium sulphate*, to be titrated with the dichromate solution. Weighs: 3.7282 grams of the dichromate are dissolved in 50 c.c. of water and 50 c.c. of dilute sulphuric acid (g). A convenient excess of ferrous ammonium sulphate (e.g., 3-4 grams), accurately weighed, is then added to the excess determined by means of the dichromate solution (b), a drop of the liquid being removed from time to time and tested with potassium cyanide. The amount of dichromate corresponding with 1 gram of ferrous ammonium sulphate is then calculated (with pure products 1 gram of the sulphate = 1.25 gram of the dichromate).

(d) *Silver carbonate*, to be prepared afresh for each operation by treating 10 c.c. of 0.5% silver sulphate solution with 4.9 c.c. of normal sodium carbonate solution, allowing the precipitate to deposit, decanting off the liquid and washing once by decantation.

(e) *Basic lead acetate*, obtained by boiling 10% neutral lead acetate solution with excess of litharge for an hour and filtering while hot.

(f) *Potassium ferricyanide* in 0.1% solution.

(g) *Dilute sulphuric acid*, conc. acid being mixed with its own volume of water.

**Procedure.** 20 grams of the sample are made up to 250 c.c. with water in a 250 c.c. flask. Of this solution, 25 c.c. are treated, in a 100 c.c. flask, with the silver carbonate (d) and, after about 10 minutes, with 5 c.c. of basic lead acetate (e), the liquid being then made up to the mark and 1.5 c.c. of extra water added to compensate for the volume of the precipitate. The whole is then shaken vigorously and filtered through a dry filter, the first 10 c.c. of filtrate being discarded and the remainder refiltered if turbid.<sup>1</sup> A small portion is tested to ascertain if fresh addition of the lead acetate is necessary. If this is the case, the above treatment is repeated.

(1:4) to precipitate the excess of lead and then with 3.7282 gram powdered dichromate (*a*) and 25 c.c. of water. When the dichromate is dissolved, 50 c.c. of the dilute sulphuric acid (*g*) are added and the solution is kept in a boiling water-bath for two hours, care being taken to prevent contamination from organic vapours (alcohol, etc.) and from dust. It is then allowed to cool, an exactly weighed amount (in excess) of ferrous ammonium sulphate (*e.g.*, 3-4 grams) being added and the extent of the excess measured by titration with the dichromate solution (*b*), potassium ferrocyanide being used, as before, as indicator.

As it is known from the titration of the ferrous ammonium sulphate (*see c*) with how much dichromate 1 gram of the ferrous salt corresponds to, the quantity of dichromate used in oxidising the glycerine, and from this the amount of the glycerine, may be calculated: 1 gram of the dichromate corresponds to = 0.13411 gram of glycerine.

As regards these two methods, adopted by the International Commission of Pure Substances, Tortelli and Ceccherelli<sup>1</sup> point out that only the second—the dichromate method—is really exact. The acetin method, according to the accurate investigations of these authors, gives inconstant and low results.

The same authors also suggest some practical modifications in the acetin method.

## B. Pure Glycerine

With pure glycerines the specific gravity is determined and common impurities (heavy metals, sulphates, chlorides, oxalates, arsenic, acrolein, formic acid, fats) and adulterations (sugar, etc.) are tested for. In some cases the chlorides are determined and positive residue at 160° and other determinations described for crude glycerine. With dynamite glycerine, a nitration test is made.

**1. Specific Gravity.**—This is determined by the Westphal balance, pycnometer or hydrometer.

If the glycerine is pure, the content of water may be calculated from the specific gravity by means of the following table (page 469).

**2. Detection of Impurities and Adulterations.**—This is determined by means of the following tests:

(*a*) 1 volume of the glycerine is dissolved in 5 vols. of water. The reaction of the solution tested with litmus paper: pure glycerine gives a neutral reaction.

Aliquot parts of the same solution are then treated with ammonium sulphide and with ammonium sulphide to ascertain if heavy metals are present (brown coloration): with barium chloride for the detection of sulphates.

# Specific Gravity of Aqueous Glycerine

Specific gravity according to		Percentage by weight of Glycerine.	Specific gravity according to		Percentage by weight of Glycerine.
at 12-14°	Gerlach at 15° Water at 15°=1		Lenz at 12-14° Water at 12°=1	Gerlach at 15° Water at 15°=1	
691	1.2653	100	1.2212	1.2184	82
664	1.2628	99	1.2185	1.2157	81
637	1.2602	98	1.2159	1.2130	80
610	1.2577	97	1.2016	1.1990	75
584	1.2552	96	1.1889	1.1850	70
557	1.2526	95	1.1733	1.1711	65
531	1.2501	94	1.1582	1.1570	60
504	1.2476	93	1.1455	1.1430	55
478	1.2451	92	1.1320	1.1290	50
451	1.2425	91	1.1183	1.1155	45
425	1.2400	90	1.1045	1.1020	40
398	1.2373	89	1.0907	1.0885	35
372	1.2346	88	1.0771	1.0750	30
345	1.2319	87	1.0635	1.0620	25
318	1.2292	86	1.0498	1.0490	20
292	1.2265	85	1.0374	—	15
265	1.2238	84	1.0245	1.0245	10
238	1.2211	83	1.0123	—	5

1 c.c. of the glycerine and 1 c.c. of ammonia are heated to 60° drops of silver nitrate solution then added: the appearance of a coloration or deposit within 5 minutes denotes the presence of *acrolein mic acid*.

1 c.c. is heated with 1 c.c. of 15% sodium hydroxide solution: evolution of ammonia indicates the presence of *ammonium* salts, or yellowing solution the presence of *glucose*. The presence of the latter may be ascertained by boiling a few drops of the glycerine with Fehling's solution (precipitate).

1 c.c. is heated gently with dilute sulphuric acid to ascertain if a pleasant rancid odour is evolved (*fatty substances*); the liquid is then neutralised and boiled with Fehling's solution (*sugar*).

1 volume of the glycerine is treated with about 2 vols. of strong alcohol: turbidity denotes presence of *gum* or *dextrin*.

A few c.c. of the glycerine are evaporated in a small dish to ascertain if any residue remains (usually *mineral substances*).

to this are carefully dropped 20 grams of the glycerine, the beak externally cooled with water meanwhile. The product is subsequently transferred, with every precaution, to a graduated cylinder and not if the nitroglycerine separates promptly and if it is pale and clear. the separation of the nitroglycerine from the acid liquid is sharp, the of the former is measured ; multiplication of this volume by 1.609 gravity of nitroglycerine at 15°) gives the weight.

\* \* \*

*Glycerine liquors* obtained directly by saponification with alkali in an autoclave contain 5-10% of glycerine, whereas those resulting from saponification by Twitchell's method or by enzymes contain 12-19%.

*Crude glycerine* (concentrated) usually contains 80-90% of glycerine with varying quantities of salts (ash), residue fixed at 160°, free acids or alkalies.

*Refined glycerine* (pure, puriss.) should be free or almost so from the impurities already mentioned (*see* Pure Glycerine, 2).

Double distilled glycerine for pharmaceutical purposes should, in part, satisfy the various tests indicated under 2.

*Dynamite glycerine* should have a specific gravity not less than 1.26, should be perfectly neutral, should contain no more than traces of chlorides (not more than 0.025% of NaCl), sulphates, lime, magnesia, alumina and reducing substances, and not more than 0.25% of residue fixed at 160°. In the test it should give not less than 200% of nitroglycerine (theoretical yield), which should separate promptly as a colourless or almost colourless, clear liquid.

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